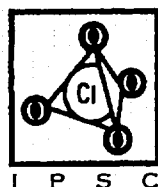


POOR LEGIBILITY

ONE OR MORE PAGES IN THIS DOCUMENT ARE DIFFICULT TO READ
DUE TO THE QUALITY OF THE ORIGINAL

Inter-Agency Perchlorate Steering Committee Stakeholder Forum

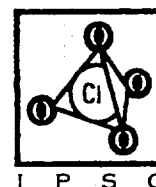


Overview and History

25-27 August, 1998

Salt Lake City, UT

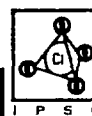
Phoenix, AZ



INFORMATIONAL BRIEFING
Lieutenant Colonel Dan Rogers, AFMC LO/JAV

Overview

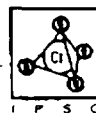
- Purpose
- Historical Information and Events
- IPSC Composition and Focus
- Forum Composition and Focus
- Where we are and Where we are going



Purpose of the Forum

- Gather together the leading experts currently working on the perchlorate issue
- Provide the public with real-time information on perchlorate projects
- Listen to public concerns

Inter-Agency Perchlorate Steering Committee

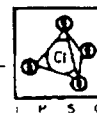


Historical Events and Chronology

(before October 1996, I couldn't spell perchlorate)

- What is Perchlorate?
- Initial Objective!
- 27 Oct 96 Cleanup and Abatement Order
- Method Detection Capability
- TERA Peer Review
- State Regulatory Partnering
- 20/21 May - Protocol Meeting and Funding
- Inter Agency Perchlorate Steering Committee

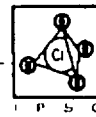
Inter-Agency Perchlorate Steering Committee



What is Perchlorate?

- **Primary Oxidizer in Solid Rockets**
 - Titan, Minuteman, Peacekeeper, Hawk, Polaris, Space Shuttle
 - Army, Navy, Air Force, NASA
- **Neither Sinker Nor Floater**
- **Very Stable in Water**

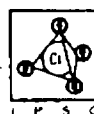
Inter-Agency Perchlorate Steering Committee



Initial Objectives

- Evaluate and Understand Potential Health Risks Associated with Perchlorate in the Environment
- To Get the Best Scientific Information on the Toxicology of Perchlorate for Use by the Decision Makers and Most Importantly to the Public
- Partner with All Stakeholders
 - DoD, Industry, Research & Regulatory Community

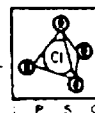
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Integrated Approach

- Analytical
- Health Effects
- Treatment Technology
- Ecological

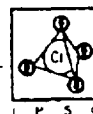
Inter-Agency Perchlorate Steering Committee



October 96
**Central Valley Regional Water Quality
Board**

- Cleanup and Abatement Order
- Emphasis on Observation of Plume Movement and Detection (MDL 400 ppb)
- Time-line for Cleanup of Groundwater
- Treatment Technology
 - Aerobic Pilot Project
 - Tyndall CRADA

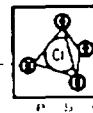
Inter-Agency Perchlorate Steering Committee



**Analytical Method Detection Limit
(or how low can you go??)**

- Pre Jan 97.....400 ppb (Aerojet)
- January 97100 ppb (Aerojet)
- April 97 4 ppb (DHS)
 - now replicated by CVRWQB, Aerojet and others
- Validation on both Aerojet and DHS Protocols by AF is Complete
- 1992/5 EPA “proposed” guidance level (4-18 ppb) based on provisional RfD

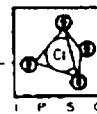
Inter-Agency Perchlorate Steering Committee



March 97 Peer Review

- Convened by TERA, Sponsored by PSG
- Overall Recommendations
 - Data insufficient
 - Solid base of studies needed
 - Minimum studies recommended
 - AF expertise recognized
- Only “known” groundwater contamination site Sacramento

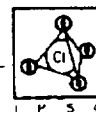
Inter-Agency Perchlorate Steering Committee



Post Peer Review Activities

- Seek study funding
- Establish protocol review process
- Expert team integration (Who?)
 - Internal (DoD)
 - External (PSG, State and Federal Researchers and Regulators)
- New source sites identified

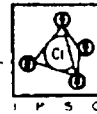
Inter-Agency Perchlorate Steering Committee



Initial State-Regulatory Partnering 21 April 97 Meeting

- Management level action officers and technical support staff
 - California DHS, DTSC, CVRWQB, OHEHA, PSG
- Partnership to serve the public
- Best value for taxpayer dollars
- Set meeting to decide best studies and protocol development

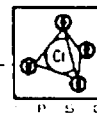
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May 1997 Perchlorate Protocol Review Meeting

- 20/21 May 1997 - Cincinnati
- Expert
 - USAF (AL/HSC/BCA), PSG, DHS, DTSC, OEHHA, EPA Superfund Office, NCEA, Ohio State, U of Cincinnati, Cytec Industries
- Goal?
 - Prioritized List of Reasonable Studies
 - Information Exchange
- California Still the Only "Site"

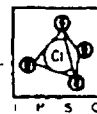
Inter-Agency Perchlorate Steering Committee



Results

- Prioritized list of studies
- Promise to assist in protocol development
- Focus on the goal without regard to cost
- Share final protocol information with the public
- Begin studies as soon as possible
- Partnering to secure needed funding

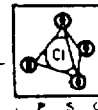
Inter-Agency Perchlorate Steering Committee



Inter Agency Perchlorate Steering Committee (13 Jan 98)

- Purpose
- Sub Committees to address critical areas
- Membership
 - Federal and State Governmental Agencies
 - Tribal Representatives
- Meetings Open to Public
- Coordinate with AWWA-RF
- Public Stakeholder Forum

Inter-Agency Perchlorate Steering Committee



Inter-Agency Perchlorate Steering Committee -as of 21 May 1998-

Executive Committee

Peter Grevatt (EPA-OSWER)
Kevin Mayer (EPA-IX)
Lt Col Dan Rogers (DoD-USAF)
Annie Jarabek (EPA-NCEA)
Mike Osinski (EPA-OW)

Ecological Impacts (T/T)

Mark Sprenger (EPA-OERR)
Cornell Long (DoD-USAF)

Health Effects/Toxicity

Dave Mattie (DoD-USAF)
Annie Jarabek (EPA-NCEA)

Analytical

Captain Dave Tsui (DoD-USAF)
Steve Pia (EPA-NERI)
Howard Okamoto (Cal-DHS)
Sanwat Chaudhuri (Utah DEQ)

Treatment Technology

Ed Urbansky (EPA-NRMRL)
Wayne Praskins (EPA-IX)
Jim Hurley (DoD-USAF)

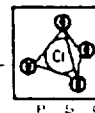
Peer Review

Peter Grevatt (EPA-OSWER)

Forum Composition and Focus

- Bring together the experts in health effects/toxicology, ecological impacts/transport and transformation, analytical methods and treatment technology
- Occurrence information
- Provide information on current initiatives
- Hear public and stakeholder concerns

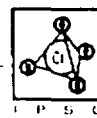
Inter-Agency Perchlorate Steering Committee



Where We Are Today?

- **Funded toxicology initiatives underway**
- **Funded treatment initiatives underway**
 - AWWA-RF
 - Air Force, Army, NASA
- **Partnership initiatives strong**
 - Liaison with States of California, Nevada and Utah, Tribal Representation
 - Expect EPA revised RfD end Sept 98 with an external peer review in Oct 98

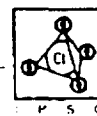
Inter-Agency Perchlorate Steering Committee



Is There a Bottom Line?

- **Goal - best scientific information to ensure protection of the nation's drinking water supply**
- **To get the best scientific information on the toxicology and occurrence of perchlorate to the decision makers and most importantly to the public**
- **Maintain an integrated approach**
- **Develop methods and technology as required**

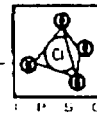
Inter-Agency Perchlorate Steering Committee



Bottom Line (continued)

- There are no limits to the success of this innovative project because of its talented and dedicated team (They don't really care who gets the credit!)

Inter-Agency Perchlorate Steering Committee



Lt Col Dan Rogers

AFMC LO/JAV

Environmental Law Directorate

4225 Logistics Ave, Ste 23

Wright Patterson AFB, Ohio 45433

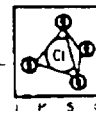
937-257-7287

937-257-0537 (fax)

drogers@jag.af.mil



Inter-Agency Perchlorate Steering Committee



PERCHLORATE OCCURRENCE

Kevin Mayer
Superfund Program
U.S. EPA, Region 9



(415) 744-2248

mayer.kevin@epamail.epa.gov

PERCHLORATE OCCURRENCE



- History - Before 1997
- Perchlorate Users
 - Facilities
 - Locations
- Perchlorate in the Environment
 - Occurrence Nationwide
 - California Wells
 - Nevada

HISTORY - Before 1997

- 1980s - Aware of Perchlorate in CA, NV
- 1985-86 - San Gabriel Valley
- 1990s - Rancho Cordova (ppm)
- 1992-95 - Provisional Reference Dose (ppb range)
- 1997 - Analytical breakthrough



San Gabriel Valley Superfund Site



- Large, complex groundwater site
- Perchlorate suspected
- Colorimetric test (0.02-0.05 mg/l) in 1985
- Preliminary data positive
- Toxicological request in Dec. 1985

San Gabriel Valley Superfund Site



- Quality Assurance Problems
 - Sample blanks - False positives
 - Cannot Validate Data
- All Perchlorate Results Rejected
- ATSDR: Better Analysis First
- No Immediate Developments in Analysis

Agency for Toxic Substances and Disease Registry - ATSDR (January 21, 1986):

"... Given the proprietary nature of the laboratory method for quantification and the poor quality assurance results noted, the data do not prove that perchlorate ion has actually been found. If the presence of perchlorate ion is confirmed, the scientific database on this ion is insufficient to generate either an acute or longer-term health advisory for drinking water"

"... The minimal acute toxicity data available suggest that one or two ppm perchlorate ion would not represent an immediately acute and substantial threat to the public health. The ATSDR does not consider this level to be "safe" in the absence of experimental data."

Aerojet General Superfund Site (Rancho Cordova)



- Perchlorate > 1 mg/l in groundwater
 - Detectable by EPA method (Ion Chromatography)
- Region 9 requests Provisional RfD from NCEA EPA Nat'l Center for Environmental Assessment
- December, 1992: 4 micrograms/liter (ppb)
- October, 1995 range: 4-18 ppb
- Analytical Limit 400 ppb

USES of PERCHLORATE

- 90% Solid Rocket Fuel Oxidizer
- Explosives
- Fireworks and Pyrotechnics
- Reported in Nitrate Fertilizer from Chile



PERCHLORATE SHIPMENTS



- Manufacturer's Information
- About 150 facilities
- 35+ States
- Most Information in Last 20 Years

PERCHLORATE in the ENVIRONMENT



- UTAH, ARKANSAS, NEW YORK wells, also MARYLAND, TEXAS
- American Water Service Survey
 - 425 wells, 7 hits (4 states)
- CALIFORNIA
 - Over 500 Water Supply Wells Tested
 - About 110 Reported, More than 30 Wells over 18 ppb

EXAMPLE FACILITIES

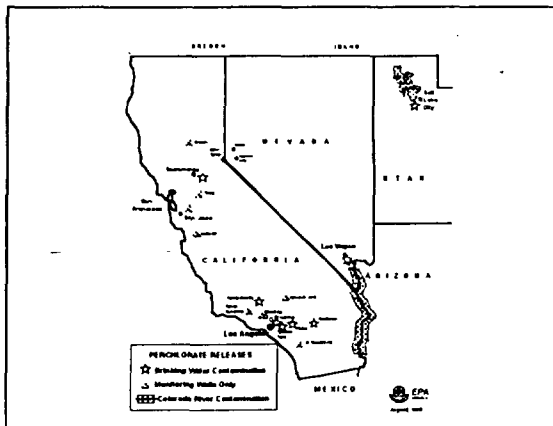


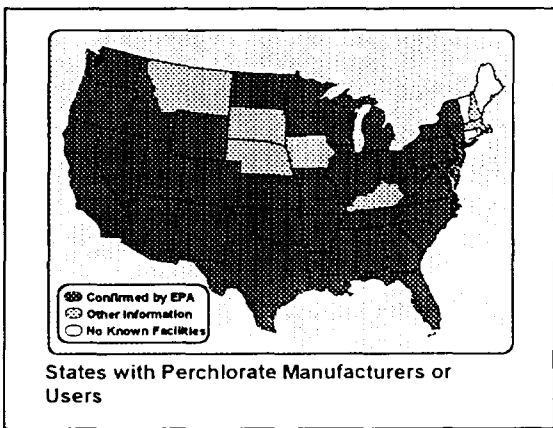
- Many Rocket Manufacturing/Testing
 - Aerojet, Lockheed, JPL
- Whittaker - Ordnance and Missiles
- Rialto - Ammunition, Fireworks and Rockets
- LLNL Site 300 - Explosives (Alpha Explosives, Lincoln CA)

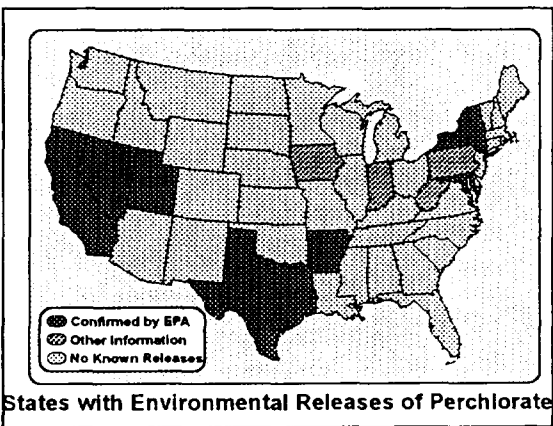
COLORADO RIVER and LAKE MEAD



- Southern California Aqueduct
- Lake Havasu (Colorado River)
- Lake Mead
- Non-Detect Upstream
- Downstream of Parker Dam









**Utah Department of Environmental Quality
Division of Solid and Hazardous Waste**

Presentation for the City of Magna

Introduction

- ▶ **Identification of the Perchlorate Problem**
 - ▶ **Initial Discovery**
 - ▶ **Notification of Regulatory Agencies**
 - ▶ **Notification of Municipal Water Users**



**Utah Department of Environmental Quality
Division of Solid and Hazardous Waste**

Presentation for the City of Magna

- ▶ **Initial Scope of Investigation**
 - ▶ **Sampling of the Kennecott Water System**
 - ▶ **Sampling of the Magna Water System**
 - ▶ **Development of a Program to Sample Private Water Well**
 - ▶ **Identification of the Private Wells**
 - ▶ **Development of a Scope of Work**
 - ▶ **Sampling**



**Utah Department of Environmental Quality
Division of Solid and Hazardous Waste**

Presentation for the City of Magna

Current Status

- ▶ **Kennecott Utah Copper's Water System**
 - ▶ **Scope**
 - ▶ **Kennecott's Initial Response**
 - ▶ **Monthly Monitoring of the System**
 - ▶ **Quarterly Monitoring of the Artesian Wells that feed Kennecott's System**



**Utah Department of Environmental Quality
Division of Solid and Hazardous Waste**

Presentation for the City of Magna

- ▶ **Alliant Techsystems**
 - ▶ **Scope of Problem**
 - ▶ **Continued Sampling of On-Site Groundwater Monitoring Wells**
 - ▶ **Installation of Additional Off-Site Monitoring Wells**
 - ▶ **Design of Interim Corrective Measure to Investigate Potential Source Areas at the Bacchus Works**



**Utah Department of Environmental Quality
Division of Solid and Hazardous Waste**

Presentation for the City of Magna

- ▶ **Magna Water Company**
 - ▶ **Monitoring of the Magna Drinking Water System**



**Utah Department of Environmental Quality
Division of Solid and Hazardous Waste**

Presentation for the City of Magna

Ongoing Studies

- ▶ **Continued Monitoring of Kennecott and Magna Drinking Water Systems**
- ▶ **Evaluation of the new Off-Site Monitoring Wells**
- ▶ **Implementation of the Interim Corrective Measure to Investigate Potential Perchlorate Source Areas and Stabilize as Appropriate**
- ▶ **Evaluate the Need and Placement of Additional Monitoring Well(s)**

ALLIANT TECHSYSTEMS
QUARTERLY GROUNDWATER MONITORING
PERCHLORATE RESULTS (ppb)

Well Number	3Q97 Results	4Q97 Results	1Q98 Results	2Q98 Results
GW-001	4	10	4	16
GW-002	NS	30	21	NS
GW-004	7	9	18	42
GW-005	65	69	72	93
GW-010	79	85	68	81
GW-012	ND	19	7	17
GW-013	47	52	ND	187
GW-014	79	97	89	99
GW-015	26	27	21	49
GW-016	146	122	59	113
GW-018	NS	81	59	NS
GW-019	65	75	47	61
GW-020	2885	1896	29312	19236
GW-024	341	263	173	314
GW-025	NS	18704	20070	NS
GW-026	ND	ND	ND	ND
GW-028	4	ND	ND	ND
GW-029	ND	ND	ND	6
GW-037	NS	ND	ND	NS
GW-038	5.2	NS	55	NS
GW-039	NS	11	12	NS
GW-040	ND	NS	ND	NS
GW-042	NS	24	NS	NS
GW-043	80	98	44	78
GW-047	NS	832	791	NS
GW-049	107	106	74	95
GW-052	NS	ND	NS	NS
GW-053	19	21	23	24
GW-056	210	207	224	247
GW-057	22	24	22	24
GW-061	NS	ND	NS	NS
GW-067	365	388	342	323
GW-068	365	358	301	354
GW-069	395	376	338	342
GW-072	205	201	169	206
GW-077	42	42	35	51
GW-078	4	ND	ND	4

NS - Not Sampled
ND - None Detected

**Alliant Techsystems Sampling Results
Kennecott's Section 21 Wells
Perchlorate**

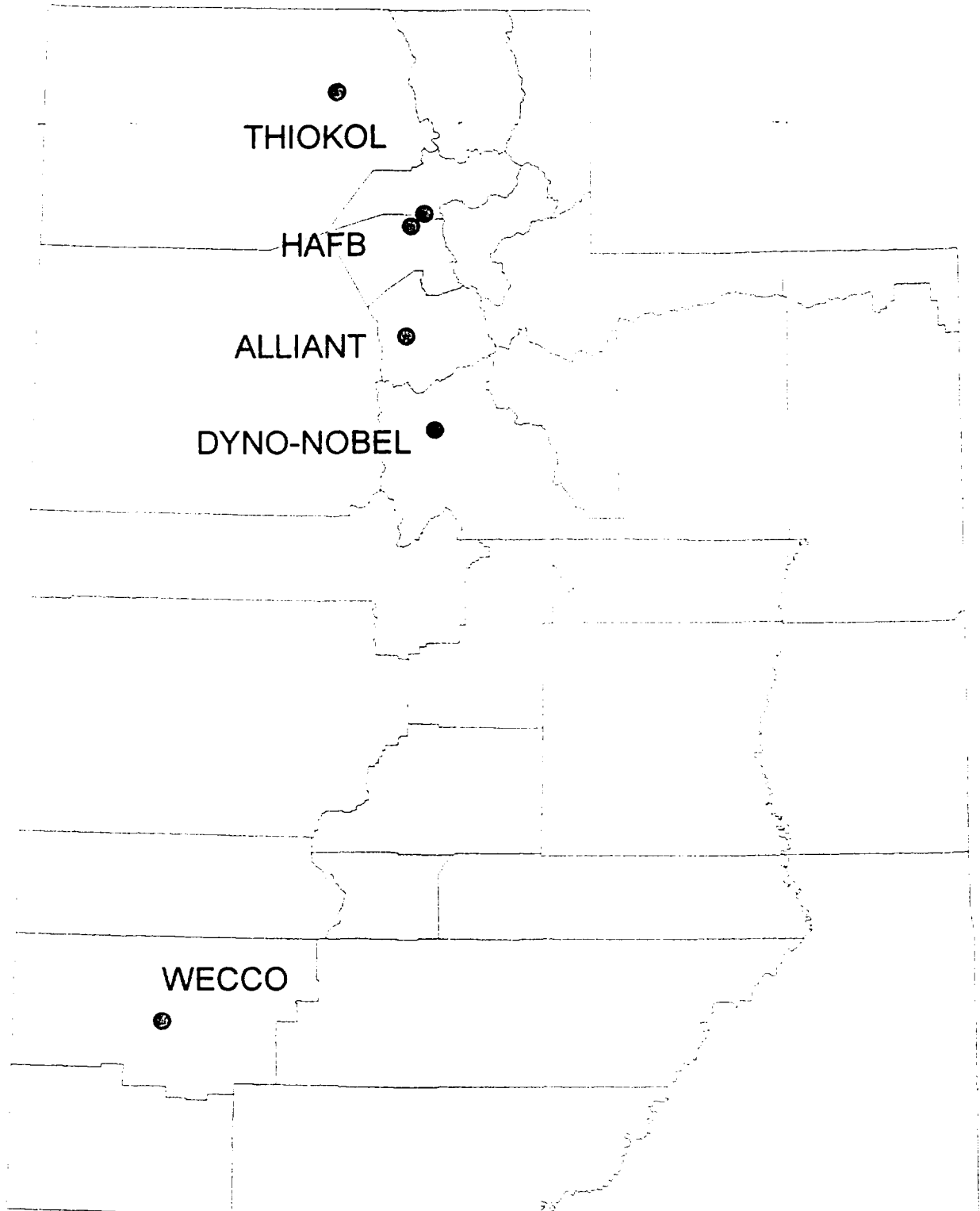
WELL NUMBER	Sept-97	Oct-97	Nov-97	Dec-97	Jan-98	Feb-98	Mar-98	April-98	Jun-98	Aug-98	COMMENTS
Well 11	21	15	NS *	NS *	13	20	NS*	NS*	20	21	See note 3, 4
Well 14	22	16	24 *	NS *	18	28	18	<4	20	20	See note 1, 2, 4
Well 15	4	<4	<4	<4	<4	<4	<4	<4	5	4	
Pump-House	13	12	10	<4	8	12	<4	<4	12	13	

ND : None detected NS: Not Sampled M: Equipment Malfunction during analysis

***Notes:**

- 1) Well 14: Was disconnected from the pumphouse when Novembers sample was taken.
- 2) Well 14: Was unable to aquire a sample for the month of December 1997.
- 3) Well 11: Was unable to aquire a sample in the months of November and December 1997, and March and April 1998.
- 4) Well 11 and 14 samples results for January 1998 were unobtainable due to GC/MS problems.

UTAH OCCURRENCE STUDY



UTAH DIVISION OF DRINKING WATER PERCHLORATE OCCURRENCE STUDY

The facilities that have used or are currently using perchlorate were identified. The direction of ground water flow around these facilities was determined, and the operational public drinking water sources in the pathway of the ground water flow were sampled for perchlorate. Perchlorate samples were collected from these sources between May and June 1998, and analyzed by the Utah State Health Laboratory. Where possible the pH and temperature readings were taken at the time of sampling. (Results attached)

Facilities in Utah: Thiokol, Hill Air Force Base, Alliant, Dyno-Nobel, WECCO

Thiokol

The ground water flows towards the Great Salt Lake. Samples were collected from the Maple/1000 Acre Spring, Sandall Well, Well #3A, Well #9, Toombs Well #11, and Well #12. All results showed <4 ug/L except for Well #3A which showed 39 ug/L perchlorate. Thiokol has previously monitored this source for perchlorate and was aware of the problem. Well #3A delivers water to an eye wash station and showers at one of the facility buildings. It is not used for drinking water, but has the possibility of coming into contact with the human body through the eye wash station and showers. The employees that work in this building have been notified and further testing is being done to monitor the contamination.

Hill Air Force Base

Ground water flows from east to west toward the Great Salt Lake. The northeast and southwest boundaries were used to delineate an area around Hill Air Force Base. All operating drinking water sources that fall within and around this boundary were sampled for perchlorate. All results were <4 ug/L.

Alliant

The ground water flows north from Alliant Techsystems. Samples were collected from the Kennecott Section 21 wells, Magna's Barton and Haynes well fields, Granger Hunter Improvement District, and the Kearns Improvement District. The only detections of perchlorate were at the Kennecott Section 21 pump house and Magna's Barton #5 Well.

Perchlorate has been detected in Kennecott's wells since September of 1997. The deep wells #14 and #11 have showed around 20ug/L of perchlorate since September of 1997 (see attached data). Well #15 results for perchlorate range from <4 ug/L to 5 ug/L. The water from these wells mixes at the pump house where perchlorate results average 12 ug/L. The water from the pump house serves this non-transient non-community system. Notices are posted above all drinking fountains and faucets at Kennecott and bottled water is provided for the employees.

Magna is currently resampling all of their wells and their distribution system for perchlorate. The latest results confirm levels of perchlorate in Baron #5 around 4 ug/L. All of the other wells in Magna's system have shown no detections of perchlorate.

Dyno-Nobel

The ground water flows towards Utah Lake. There are no public drinking water sources down stream of Dyno-Nobel. However, there are three private wells in the area that have been tested and shown no detections of perchlorate.

Western Electrochemical Company (WECCO)

The ground water flows in a north west direction from the facility. There are only three drinking water sources in this pathway. These are the three drinking water wells for WECCO. Only Well #1 is currently in use and showed <4 ug/L perchlorate in the May sample.

There are three perchlorate contaminated drinking water sources in Utah: Kennecott at 13 ug/L, Thiokol at 39 ug/L (but not used for drinking), and Magna's Barton #5 near 4ug/L. In no case is water being delivered for consumption above the California Department of Health Services provisional level of 18 ug/L. All contaminated sites are continually being monitored for perchlorate.

**UTAH DRINKING WATER OCCURRENCE STUDY
RESULTS**

SYSTEM	SOURCE	ClO4	pH	Temp.	NO3	Br	I	SO4	Cl	TDS
Kearns ID	#9 4550 S 6000 W	<4								
	Well #12	<4								
Kennecott	Well #11	<4								
	Well #14	<4								
	Well #15	<4								
	Pump House	15								
Thiokol	Maple/1000 Acre	<4								
	Sandall Well	<4								
	Well #3A	39								
	Well #9	<4								
	Toombs Well #11	<4								
	Well #12	<4								
HAFB	Well No. 2	NIU								
	Well No. 3	<4	7.4							
	Well No. 6	NIU								
	Well No. 7	NIU								
	Well No. 8	<4	7.4							
	Well No. 9	<4	7.4							
WECCO	Wecco Well #1	<4								
Granger-Hunter ID	#5 2400 S 3600 W	<4			<1	<0.2	<1	105.00	142.0	524
Magna	Barton #1	<4								
	Barton #2	<4								
	Barton #3	<4								
	Barton #4	<4								
	Barton #5	5.3								
	Haynes #1	NIU								
	Haynes #2	NIU								
	Haynes #3	NIU								

UTAH DRINKING WATER OCCURRENCE STUDY RESULTS

SYSTEM	SOURCE	ClO4 ⁻	pH	Temp.	NO3	Br	I	SO4	Cl	TDS
	Haynes #4	<4								
	Haynes #5	NIU								
	Haynes #6	<4								
	Haynes #7	<4								
	Haynes #8	<4								
WB WCD/Davis	Laytona Well	<4	7.07	14	1.621	0.045	<1	27.390	26.230	330
	Fairfield Well	NIU								
	Clearfield Well No.2	NIU								
WB WCD/Weber	So. Weber No. 1	<4	6.81	23	0.709	0.037	<1	16.550	31.600	262
	Dist. Well No. 2	NIU								
	Dist. Well No. 3	NIU								
Roy	5175 S 2425 W	<4	7.6	15	0.885	0.024	<1	24.593	18.898	
Riverdale	5190 S 1050 W #1	<4		16.6	0.678	0.026	<1	18.676	17.221	244
Hooper Water ID	Well #1 5450 South	<4	7.6		0.853	0.025	<1	21.176	16.623	
Clinton	Clinton Well	<4	7.21	16	2.708	0.025	<1	28.206	16.331	292
West Point	Well #1	<4	7.6	10	0.746	20.13	<1	20.130	18.970	288
	Well #3	<4	7.6	10	2.12	<0.25	<1	21.000	17.000	312
Layton	Hillfield Well	<4	4.5	14.3	2.276	<0.25	<1	22.120	18.719	262
	Sandridge #2	<4	4.3	16.7	1.423	0.042	<1	26.950	29.940	328
Clearfield	Reservoir Well	<4								328
	Freeport #1	<4								304
	At Hill AFB Well	<4								284

NIU: Not In Use

**Alliant Techsystems Sampling Results
Kennecott's Section 21 Wells
Perchlorate**

WELL NUMBER	Sept-97	Oct-97	Nov-97	Dec-97	Jan-98	Feb-98	Mar-98	April-98	Jun-98	Aug-98	COMMENTS
Well 11	21	15	NS *	NS *	13	20	NS*	NS*	20	21	See note 3, 4
Well 14	22	16	24 *	NS *	18	28	18	<4	20	20	See note 1, 2, 4
Well 15	4	<4	<4	<4	<4	<4	<4	<4	5	4	
Pump-House	13	12	10	<4	8	12	<4	<4	12	13	

ND : None detected NS: Not Sampled M: Equipment Malfunction during analysis

***Notes:**

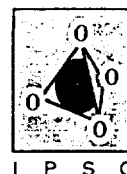
- 1) Well 14: Was disconnected from the pumphouse when Novembers sample was taken.
- 2) Well 14: Was unable to aquire a sample for the month of December 1997.
- 3) Well 11: Was unable to aquire a sample in the months of November and December 1997, and March and April 1998.
- 4) Well 11 and 14 samples results for January 1998 were unobtainable due to GC/MS problems.

Testing Strategy and the Revised RfD / Risk Assessment

Annie M. Jarabek
National Center for Environmental Assessment
U.S. Environmental Protection Agency



Perchlorate Stakeholders Forums
Sponsored by the IPSC
Salt Lake City, UT and Phoenix, AZ
August 25 and August 27, 1998



The Perchlorate Contamination Challenge Credible Science



Credible Decisions

- Accurate risk characterization
- Appropriate management strategies

The Perchlorate Contamination Challenge

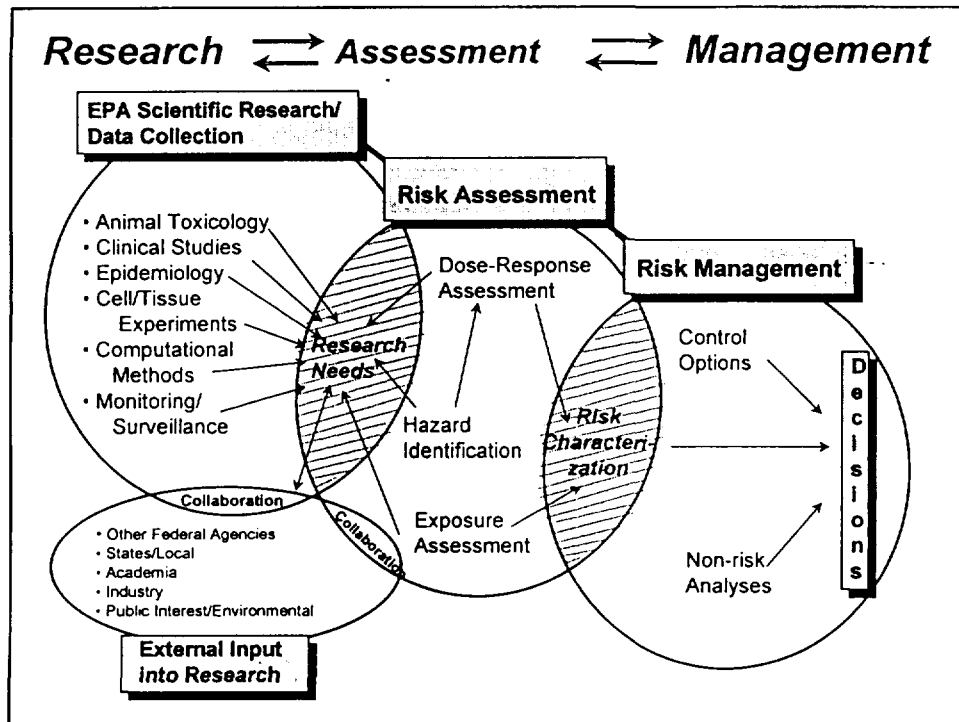
An Integrated Approach

- Occurrence survey
- Stakeholder issues
- Health effects / toxicology
- Analytical methods (detection limit)
- Ecological impact / transport and transformation
- Treatment technology
- Technology transfer

The Perchlorate Contamination Challenge

Pro-Active Partnership

- Unprecedented timeframe
- Targeted expertise



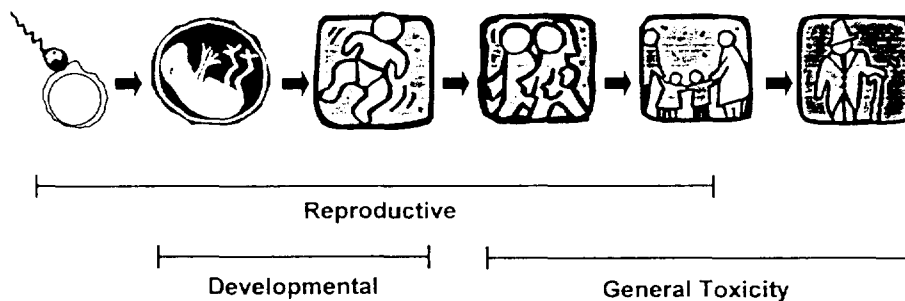
Outline

- **Background**
 - Definition of the RfD
 - Derivation of the RfD
 - Basis of the provisional RfD
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- **Recommended new studies**
 - Description of different study designs
 - Objectives of each study
 - Strategy for synthesis of data
- **Summary**

Definition

An oral reference dose (RfD) is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime.

A High Confidence RfD is Based on Data that Addresses All Potentially Critical Life Stages.

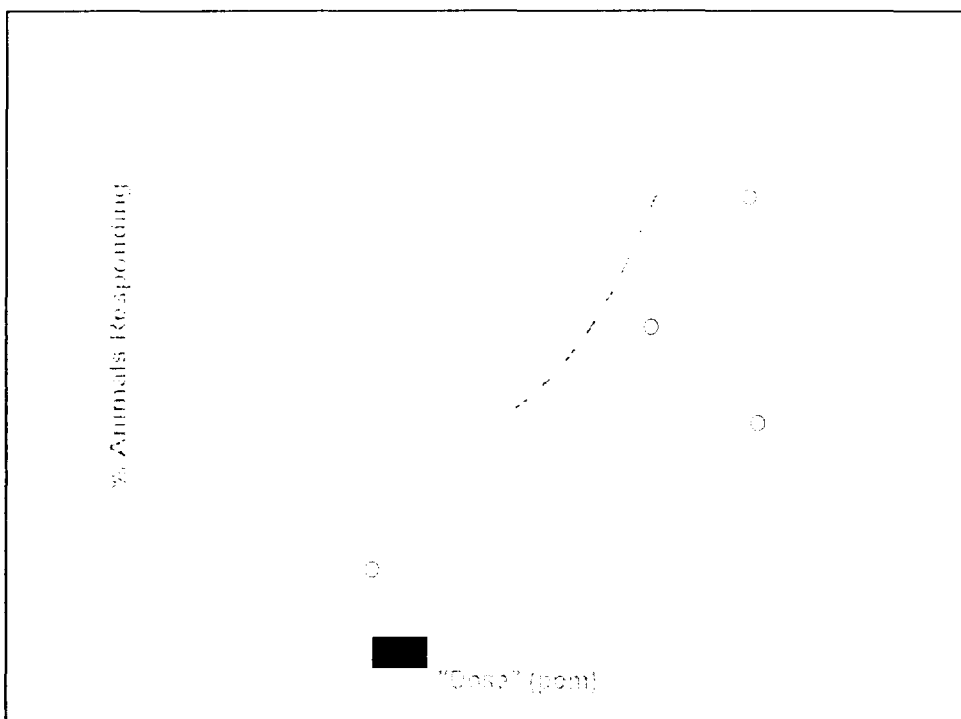
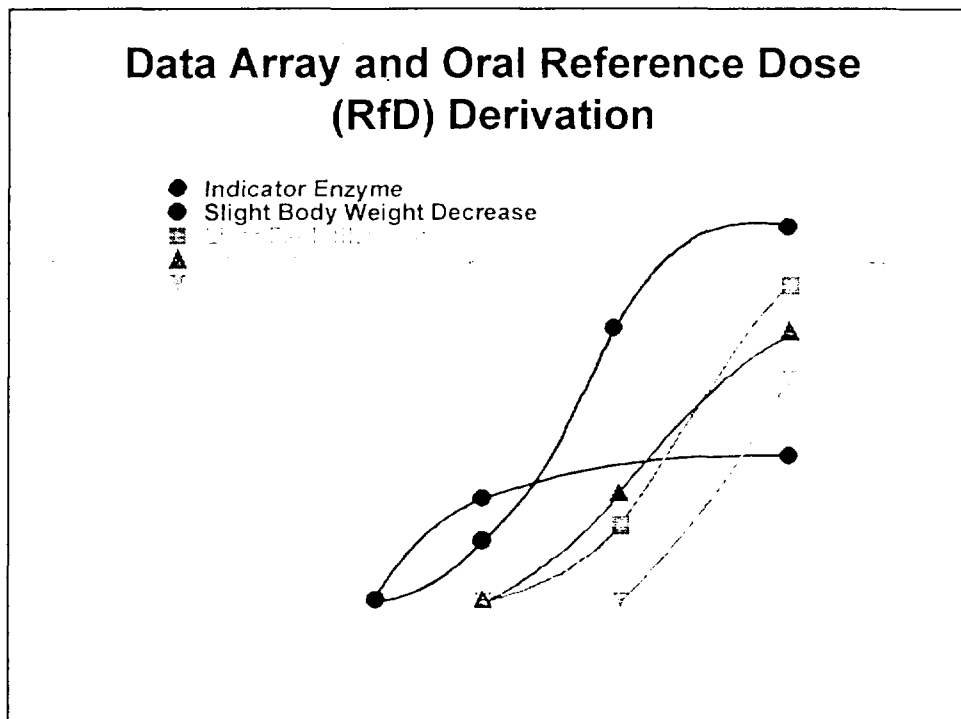


Minimum Data Base for Derivation of an RfD

- * Rationale is to address all potentially critical life stages
- ** Rationale is to use different species to evaluate variability in species sensitivity unless a particular laboratory animal model is more appropriate

RfD Derivation

- Hazard identification and data array analysis
- Designation of effect levels (NOAEL, BMD)
- Choice of critical effect
- Dosimetric adjustment
- Application of uncertainty factors (UF)
- Characterization of uncertainty (confidence levels)



$$RfD = \frac{NOAEL * [HED]}{UF \times MF}$$

Where:

NOAEL*[HED] =

The NOAEL or equivalent effect level obtained with an alternate approach (*), dosimetrically-adjusted to a human equivalent dose [HED].

UF =

Uncertainty factor(s) applied to account for the extrapolation required from the characteristics of the experimental regimen to the assumed human scenario, and

MF =

Modifying factor to account for scientific uncertainties in the study(ies) chosen as the basis for the operational derivation, e.g., poor statistical power or exposure characterization.

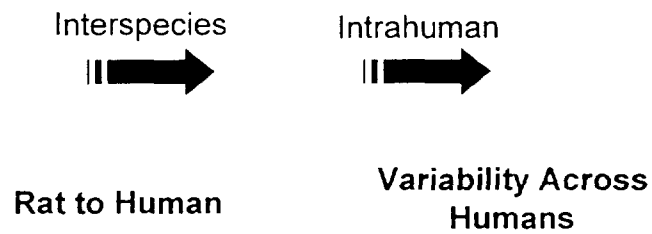
Factors for Uncertainties in Applied Extrapolations

- 10_H Human to Sensitive Human
- 10_A Experimental Animal to Human
- 10_S Subchronic to Chronic Duration
- 10_L LOAEL(HEC) to NOAEL(HEC)
- 10_D Incomplete to Complete Data Base

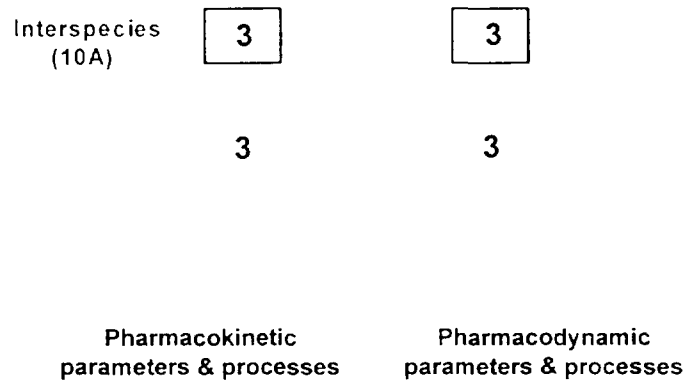
Modifying Factor

MF Professional Assessment of Scientific Uncertainties of the Study and Data Base not Explicitly Addressed Above. Default for the MF is 1.0 e.g., applied for small sample size or poor exposure characterization.

Extrapolation Uncertainties



Schematic of UF Components Incorporated Into Exposure-Dose-Response Characterization



Basis of the Provisional RfD

- Initial correspondence to EPA Region IX (Dec 92) from Superfund Health Risk Technical Support Center (NCEA-Cin)
- Principal study = Stanbury & Wyngaarden (1952)
- NOAEL = 0.14 mg/kg-day for 100% iodide release
- UF = 1000
 - intrahuman variability (10)
 - less than chronic data (10)
 - database deficiencies (10)
- Drinking water criteria = 3.5 ppb based on 70 kg / 2 L water

Second Provisional RfD (1995)

- Revision based on PSG submission to Superfund Health Risk Technical Support Center (NCEA-Cin)
- Same principal study and NOAEL
- Different UF
 - intrahuman variability (10)
 - less than chronic data (10)
 - database deficiencies decreased (3)
- Drinking water criteria = 18 ppb based on 70 kg / 2 L water

**Provisional RfD
March 1997
External Peer Review**

- **Proposed by TERA**
- **Same principal study, critical effect**
- **Another, different UF = 100**
 - intrahuman reduced (3)
 - subchronic to chronic (3)
 - LOAEL to NOAEL (3)
 - Database deficiencies (3)

**March 1997
External Peer Review**

- **Inadequate data base for RfD derivation**
- **Available mechanistic insights suggest special studies and synthesis strategy**
- **Eight (8) additional new categories of studies recommended**

Deficiencies of Clinical Data

- **Adult subjects**
- **Typically subjects with thyroids altered by disease or other treatments**
- **Few pregnant subjects**
- **Acute or short-term exposure duration**
- **Limited range of doses**

Susceptibility

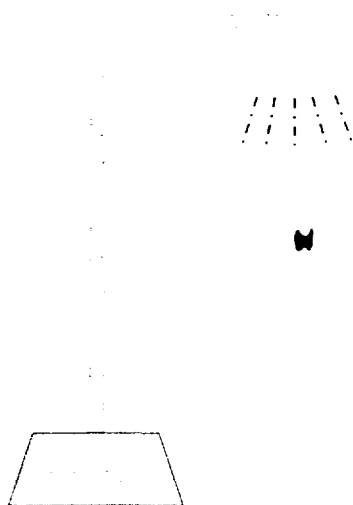
The potential for increased susceptibility is due to factors that influence:

- (1) **Exposure e.g., activity patterns and location**
- (2) **Deposition / uptake and the internal target tissue dose (i.e., pharmacokinetic parameters) and toxicant-target interactions, e.g., metabolism rates or pathways**
- (3) **Tissue sensitivity (pharmacodynamics) - conditions which alter or enhance target tissue response, e.g., age, nutritional status, or disease states**

Outline

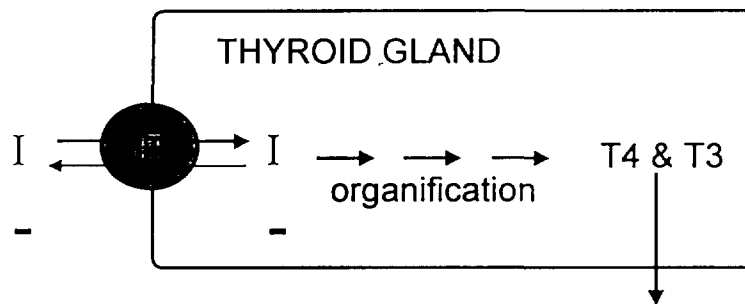
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Established Perchlorate Toxicity



The only systematically studied and established effect is the anti-thyroid effect due to competitive inhibition of iodine uptake.

Iodine and the Thyroid Gland



National Health and Environmental Effects Laboratory



Main Symptoms/Effects of Hypothyroidism

Developmental

- delayed reflex ontogeny
- impaired fine motor skills
- deaf-mutism, spasticity
- gait disturbances
- mental retardation
- speech impairments

*transient disruption leads
to permanent effects*

Adult

- run down, slow, depressed,
- sluggish, cold, tired
- dryness and brittleness of hair
- dry and itchy skin, constipation
- muscle cramps
- increased menstrual flow

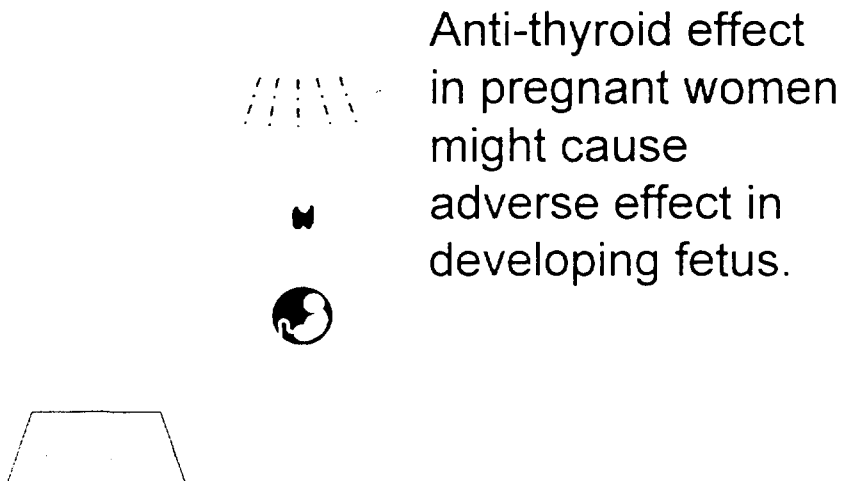
*transient disruption leads to
transient effects*

*thyroid tumors in rodents

National Health and Environmental Effects Laboratory

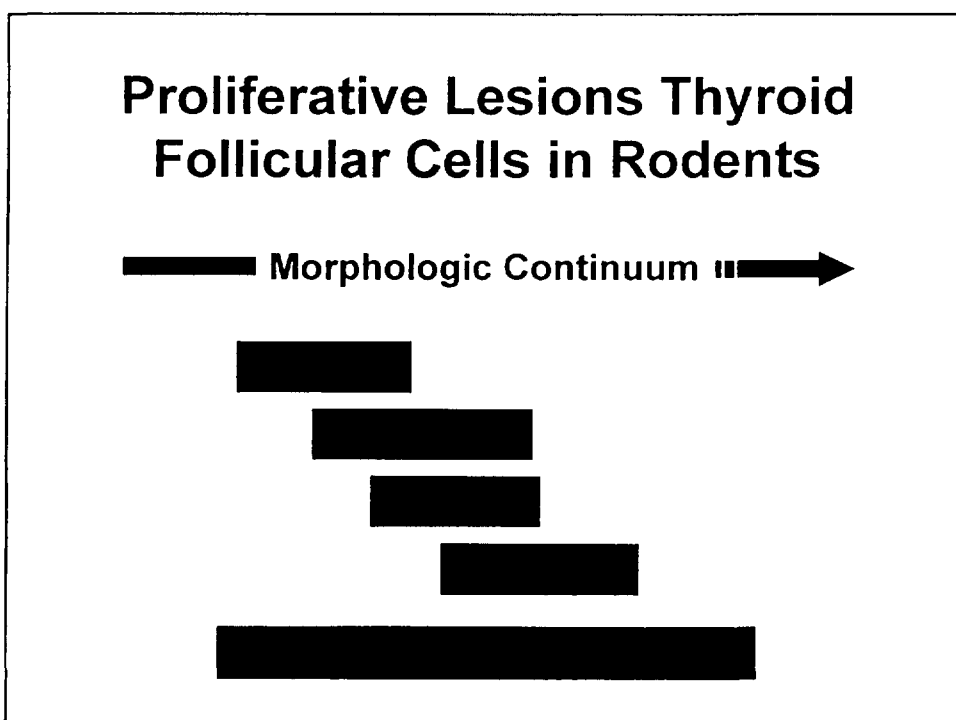
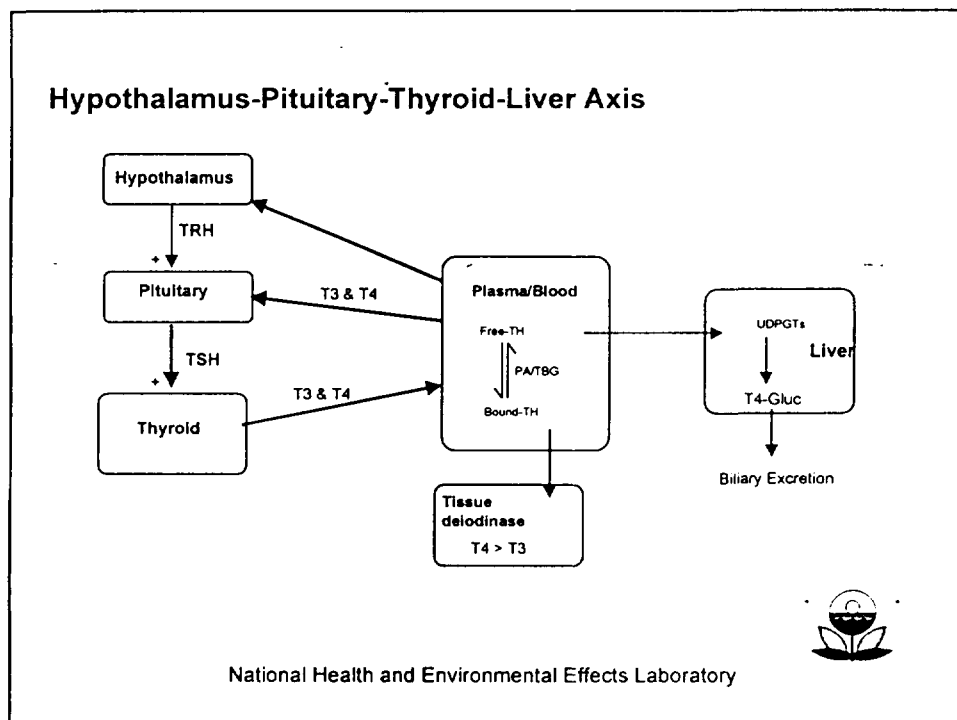


Potential Perchlorate Toxicity



Mechanisms of Anti-Thyroid Mediated Neoplasia in Rodents

- DNA Directed:
 - X - rays
 - ^{131}I
 - Genotoxic chemicals
- Indirect
 - Partial thyroidectomy
 - Transplantation of TSH-secreting pituitary tumors
 - Iodide deficiency
 - Chemicals inhibiting iodide uptake
 - Chemicals inhibiting thyroid peroxidase
 - Chemicals inhibiting TH
 - Chemicals inhibiting conversion of T3 & T4
 - Chemical inhibiting hepatic thyroid hormone metabolism and excretion



Mode of Action Provides Important Insight to Characterization of Toxicity

- A chemical's influence on the molecular, cellular, and physiological functions in producing tumors
- Prolonged depression of TH causes a feedback that leads to upregulation of TSH which leads to thyroid gland hyperplasia
- Genotoxic?

Additional Suggested Target Tissues

- Reproductive function
- Immune function
 - aplastic anemia
 - leukopenia

Existing Data Summary

- Target tissue appears to be the thyroid but available testing not comprehensive across endpoints
- Anti-thyroid effects would differ among adult versus developing fetus, children
- Anti-thyroid effects associated with benign neoplasia development in rats; a nonlinear process
- Genotoxicity not characterized
- Relevancy to human risk of rat tumors not established; presumed protective

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Recommended Studies

- 90-Day subchronic bioassay
- Developmental neurotoxicity study
- Genotoxicity assays
- Mechanistic studies
- ADME - Absorption, Distribution, Metabolism and Elimination
- Developmental study
- 2-Generation reproductive toxicity study
- Immunotoxicity

EPA Risk Assessment Guidelines

- Principles and procedures to frame the conduct of risk assessments
- Promote consistency and technical quality of scientific inferences
- Flexible, full consideration to all relevant scientific information case-by-case
- Revised as experience and scientific consensus evolve

EPA Risk Assessment Guidelines

- Developmental toxicity (1991)
FR 56(234): 63798 - 63826
- Reproductive toxicity (1997)
EPA No. EPA/630/R-96/009a
NTIS PB97-100093
- Neurotoxicity (1998)
EPA No. EPA/630/R-95/001Fa
NTIS PB98-117831
- Thyroid follicular cell tumors (1998)
EPA/630/R-97-002

EPA Perchlorate Toxicity Risk Assessment Team

- | | | |
|--------------------|--------|--|
| • Harlal Choudhury | NCEA | General toxicology / risk assessment |
| • Eric Clegg | NCEA | Reproductive toxicology |
| • Kevin Crofton | NHEERL | Neurotoxicology |
| • Vicki Dellarco | OW | Genetic toxicology |
| • Annie Jarabek | NCEA | General toxicology / dosimetry / risk assessment |
| • Gary Kimmel | NCEA | Developmental toxicology |
| • Ralph Smialowicz | NHEERL | Immunotoxicology |

Toxicity Study Review and Revised RfD / Risk Assessment

- Review of existing and new toxicity data
- Hazard identification
- Dose-response evaluation
 - Designation of effect levels (mathematical modeling or NOAEL / LOAEL procedure)
 - UF assignment
 - Uncertainty characterization - confidence statements

90-Day Subchronic Bioassay

- Tests for additional target tissues
- Minimum database for RfD derivation
- Added additional tests for:
 - reproductive parameters
 - mutagenic effects in bone marrow
 - thyroid hormone levels
- Objective is to ascertain if anti-thyroid effect is critical and its dose-response

Developmental Neurotoxicity Study in Rats

- Examines potentially critical effect and population: evaluates nervous system (structure and function) of fetal, newborn, and young animals
- Added thyroid histopathology and thyroid hormone level determinations to characterize anti-thyroid effect in offspring

Genotoxicity Battery

- Tests for toxicity to DNA in various assays
- Provides mode-of-action information to evaluate potential for carcinogenicity
- May impact consideration of uncertainty factor for less than chronic data

Immunotoxicity Study

- Evaluates immune system structure and function
- Motivated by case reports of aplastic anemia and leukopenia
- May reduce UF for database deficiencies if not critical effect

Developmental Study in Rabbits

- Endpoint required for greater confidence in database, may reduce UF for data deficiencies if not critical effect
- Definitive test for toxicity during organ development (birth defects)
- Added hormone analysis and thyroid histopathology to evaluate second species

2-Generation Reproductive Toxicity Study

- Evaluates fertility of adults and viability of (toxicity in) offspring in rats
- Tests for reproductive parameters over two generations
- Added analysis of thyroid hormones and thyroid histopathology at various time points
- Endpoint required for greater confidence in database, may reduce UF for database deficiencies if not critical effect

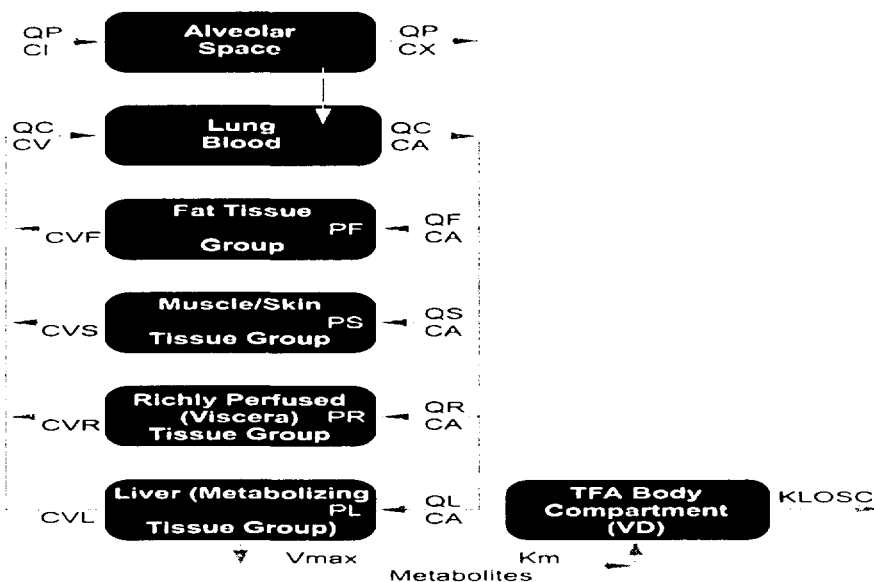
ADME study

- Literature review of perchlorate discharge test
- Protocols proposed to evaluate perchlorate kinetics, iodine inhibition kinetics and thyroid hormone homeostasis
- Basis for development of physiologically-based pharmacokinetic (PBPK) model

Mechanistic Studies

- Aid to quantitative interspecies extrapolation - basis to extend PBPK model
- Additional developmental studies to evaluate thyroid TH in fetal and post-natal periods
- Determine relative sensitivity of fetal/postnatal thyroid versus adult
- Determine relative sensitivity of rat versus human

PBPK Model Schematic



Outline

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 - Strategy for synthesis of data
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Greatest Assessment Difficulty: Designation of Adversity

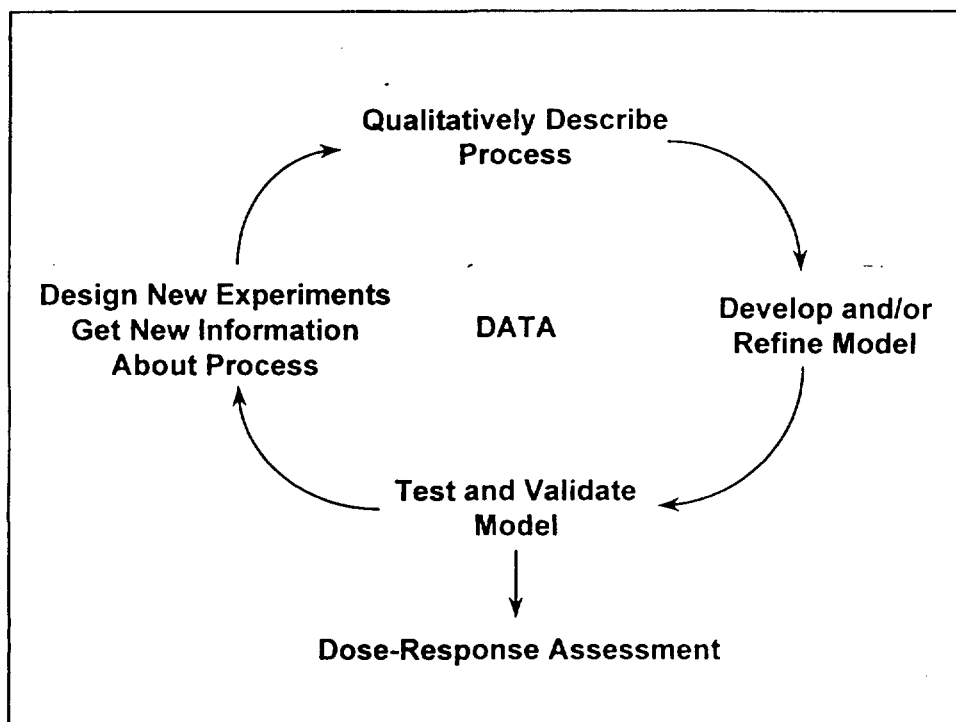
- Reversible effects in adults versus permanent deficits in developing fetus
- How can thyroid hormone data inform interpretation of adverse levels for both effects?

Revised RfD / Risk Assessment Review Process

- Internal peer review (October 1998)
- External peer review (November 1998)
- Response / revisions subsequent to external peer review (December 1998)
- Submit final revised RfD / risk assessment to Integrated Risk Information System (IRIS) process
- Refine as required with new data

Revised RfD

- Toxicity bioassay data across comprehensive array of endpoints to establish target tissue
- Mechanistically-motivated special studies to characterize critical dose-response relationships
- New occupational and epidemiology surveys
- Future refinements as required by new data



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Development, QA/QC and Status of Study Protocols

David R. Mattie, PhD, DABT
Operational Toxicology Branch
AFRL/HEST

Perchlorate Stakeholders Forum
Sponsored by the IPSC
Salt Lake City, UT and Phoenix, AZ
August 25 and 27, 1998



Required for All Recommended Studies

- **Good Laboratory Practice Standards
EPA (40 CFR Part 792)**
- **Animal Housing and Care Based on
Association for Assessment and
Accreditation of Laboratory Animal
Care (AAALAC) and Guide for the Use
of Laboratory Animals (NIH Publication
No. 96-03, 1996)**



Standard Operating Procedures

- Protocol review by expert panel
- EPA guideline testing requirements
- Standardized QA/QC process



QA/QC Procedures Air Force Sponsored Studies

- Contract lab delivers draft report to AFRL for review by contract monitor and project director
- Review includes:
 - QA/QC to confirm study conducted according to protocol requirements
 - Contractual review for form and contract requirements



QA/QC Procedures Air Force Sponsored Studies

- **Comments returned to contract lab**
 - Editorial, contractual, format
- **Contract lab addresses comments**
- **Final draft to AFRL for technical review by Senior Scientist and associates with necessary expertise**
- **Contractor addresses final comments**
- **Final report delivered to AFRL**
- **AFRL sends to EPA/NCEA within 48 hours**



QA/QC Procedures PSG Sponsored Studies

- **Contract lab delivers draft report to TERA/PSG for review by contract monitor**
- **Review includes:**
 - QA/QC to confirm study conducted according to protocol requirements
 - Contractual review for form and contract requirements
 - Editorial, contractual, format



QA/QC Procedures PSG Sponsored Studies

- Draft report undergoes technical review by AFRL Senior scientist and associates with necessary expertise
- Contractor addresses all comments
- Final report delivered to TERA/PSG
- TERA/PSG sends to EPA/NCEA within 48 hours



QA/QC Procedures Summary

- Standardized review process for all studies
- Technical review by AF Senior Scientist team
- Commitment to expedited review process to accommodate assessment schedule



Report Status

- **Completed Final Reports available for EPA/NCEA assessment:**
 - 90-Day bioassay (5/98)
 - Developmental neurotoxicity study (6/98)
 - Genotoxicity battery (7/98)
 - Developmental study (9/98)



Report Status

- **Completed Interim reports available for EPA/NCEA assessment:**
 - ADME / Mechanistic (9/98 through 5/99). Final PBPK model due 9/99.
 - 2-Generation reproductive (9/1/98: PO and F1 generation; F2 and Final report 2/98)
 - 8. Immunotoxicity (14-, 90-, and 120-day assays on 8/3/98; host resistance and tumor models 11/98)



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Peer Review of Perchlorate Risk Assessment

Peter Grevatt, Ph.D., U.S. EPA HQ

Presentation Goals

- Define Peer Review
- EPA Peer Review Policy
- Purpose of Peer Review
- Scope of Peer Review for Perchlorate
- Impact on Perchlorate Risk Assessment

Define Peer Review

- *"Documented critical review of Agency scientific or technical work product"*
 - In-depth Assessment
 - Conducted by qualified individuals
 - Independent of those who performed work
 - Equivalent in technical expertise

EPA Peer Review Policy

- *"Major scientifically and technically based work products related to Agency decisions should be peer reviewed..."*
- *"For those work products that are intended to support the most important decisions or that have special importance in their own right, external peer review is the procedure of choice..."*

Purpose of Peer Review

- Ensure quality, credible Agency decisions
- Preparation of sound, technically defensible analyses and work products.

Scope of Perchlorate Peer Review

- Independent, external peer review of all aspects of the perchlorate risk assessment
- EPA Office of Solid Waste and Emergency Response will oversee peer review
 - Study protocols
 - Study results
 - Development of reference dose
 - Selection of critical endpoint
 - Use of uncertainty factors
 - Risk characterization

Scope of Perchlorate Peer Review

- Stakeholder participation
 - Nomination of expert peer reviewers
 - Selection by independent scientific panel
 - Examination of potential conflict of interest
 - Open peer review panel meeting
 - Opportunity for comment by interested parties
 - Preparation of final peer review report

Impact on Perchlorate Risk Assessment

- Submit Final Peer Review Report to NCEA
- Preparation of Responsiveness Summary
 - Detailed response to all peer review comments
 - Comments addressed
 - Explanation of Changes
- Completion of final risk assessment

Where to reach me!

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The Safe Drinking Water Act and Perchlorate

MIKE OSINSKI
Office of Ground Water and Drinking Water
U.S. Environmental Protection Agency
Washington, D.C.

202-260-6252 202-260-3762 (fax)
OSINSKI.MICHAEL@epamail.epa.gov

Contaminant Identification and Selection Under the SDWA

- **Contaminant Selection Under the 1986 Amendments to SDWA:**
 - ⇒ Regulate 83 contaminants by 1989;
 - ⇒ Regulate 25 contaminants every 3 years.
- **Congress, EPA had Implementation Concerns:**
 - ⇒ Missed statutory deadlines;
 - ⇒ Water systems encountered difficulty in timely compliance;
 - ⇒ Focus on sound science and contaminants posing greatest risk.

Contaminant Identification and Selection Under the SDWA

- **Contaminant Selection Under the 1996 Amendments to SDWA.**
 - ⇒ Publish a Contaminant Candidate List (CCL) of contaminants known or anticipated to occur in DW and not subject to NPDWRs by Feb 1998.
 - ⇒ Broad consultation with stakeholders, NDWAC, and SAB.

Contaminant Identification and Selection under the SDWA

- **Draft CCL Published on Oct 6, 1997.**
 - Did not include perchlorate, but sought comment on whether to include it on the final CCL.
 - Public comments indicated overall support for adding perchlorate to the CCL.
- **Final CCL published on March 2, 1998.**
 - Contains 50 chemical and 10 microbiological contaminants.

Contaminant Candidate List (CCL)

- **Functions of the CCL:**
 - Make determinations for at least 5 contaminants of whether or not to regulate with a NPDWR by 2001.
 - Focus and prioritize research agenda for contaminants with data gaps.
 - Source for selection of contaminants for unregulated contaminant monitoring regulation (UCMR) due in 1999.

Perchlorate and the CCL

- **Two categories of contaminants on the CCL:**
 - (1) Regulatory Determination Priorities;
 - (2) Research Priorities.
- **Perchlorate falls into the research priorities category due to extensive data gaps in:**
 - Occurrence; health effects, treatment technologies, and analytical methods research.

Regulatory and Policy Agenda for Perchlorate

- **Determination to regulate not likely by 2001.**
 - ⇒ Extensive data gaps in all areas.
- **EPA is not currently planning to include perchlorate as a contaminant in the proposed UCMR (Fall 1998).**
 - ⇒ Lack of EPA approved analytical method(s).
 - ⇒ Recommend near-term special occurrence studies.

Next Steps for Perchlorate

- **Perchlorate is a research and occurrence priority for the OGWDW.**
 - ⇒ In process of developing short and longer term research plans on health, treatment, and analytical methods.
- **OGWDW is very engaged in the IPSC.**
 - ⇒ Ensure exchange of scientific information to support decision making based on sound science and stakeholder involvement.

Next Steps for Perchlorate

- **Possible Scenarios:**
 - (1) **Longer Term (3 to 5 years):**
 - ⇒ Data gaps filled and perchlorate moves to the regulatory determination priority category of next CCL -- due in 2003.
 - (2) **Near Term (1-2 years):**
 - ⇒ If health effects and occurrence data warrant, develop a Health Advisory.

EPA Health Advisory Program

- **SDWA General Authority:**
 - “The Administrator may publish health advisories (HA), which are not regulations, or take other appropriate actions for contaminants not subject to any national primary drinking water regulation.”
- **HAs represent concentrations of contaminant in drinking water which adverse health effects are not expected to occur.**

EPA Health Advisory Program

- **Not federally enforceable.**
- **Subject to change as new information becomes available.**
- **Can serve as technical guidance to assist State, Tribal, and local officials responsible for protection of public health.**

EPA Health Advisory Program

- **HAs used in emergency situations and describe concentrations of a contaminant at which adverse non-carcinogenic effects are not anticipated to occur following exposures:**
 - 1-day
 - 10-day :
 - Longer term (i.e. 7 years)
 - Lifetime

Sample HA Calculations

- Determine RfD in mg/kg/day.
- Determine DWEL (Drinking Water Equivalent Level) in mg/L, assuming 100% drinking water contribution.
- Determine HA in mg/L.

Sample HA Calculations

- $$\text{DWEL (mg/L)} = \frac{\text{RfD}(70 \text{ kg adult})^*}{(2 \text{ L/day})}$$
$$\text{DWEL (mg/L)} = \frac{\text{RfD}(10 \text{ kg child})^{**}}{(1 \text{ L/day})}$$

* for lifetime HA
** for 1 day, 10 day, and longer term HA
- $$\text{HA (mg/L)} = (\text{DWEL})(\% \text{ DW contribution})$$

David T. Tsui, Capt., USAF	
Air Force Research Laboratory Toxicology Branch Wright-Patterson AFB, OH	
Sanwat Chaudhuri, Ph. D. Steve Dickson	
Utah Department of Health	
8/25/98	1

IPSC Analytical Chemistry Method Sub-Committee	
<ul style="list-style-type: none">◆ Sanwat Chaudhuri, UDOH◆ Howard Okamoto, CDHS◆ Steve Pia, USEPA-NERL◆ David Tsui, AFRL/HES	
	2

Topics

- ◆ Perchlorate Analysis
 - ◆ Chemistry of Perchlorate
 - ◆ Analytical Techniques
 - ◆ Ion Chromatography (IC)
- ◆ Method Parameter Studies
- ◆ Stability Study
- ◆ Inter-laboratory Study on the Performance of IC Methods
- ◆ Anion Interference Study - AS-11

3

Chemistry of Perchlorate

- ◆ Oxidation: + 7
- ◆ Structure: sp^3 , T_d
- ◆ ClO_4^- is a Very Weak Base of $HClO_4$
- ◆ $HClO_4$ is a Very Strong Acid
 - ◆ Thermodynamically and Kinetically Unstable
- ◆ ClO_4^- is a "Polarizable" Anion
 - ◆ Low Hydration Energy
 - ◆ Small Hydrated Radius (hydrophobic)
 - ◆ Strong Interactions with π Electrons
- ◆ Perchlorate Salts are Soluble in Water

4

Solubility of Perchlorate Salts

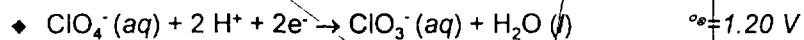
◆	Mol Wt.	Cold (g/L)	Hot (g/L)
◆ Ammonium	101.49	2.87	11.5
◆ Sodium	122.44	s.	v.s.
◆ Potassium	138.55	0.075	2.18
◆ Magnesium	223.21	9.93	v.s.
◆ Calcium	238.98	18.86	v.s.
◆ Aluminum	433.43	s.	s.
◆ Nickel	365.68	22.25	27.37
◆ Lead	460.15	49.97	n.a.
◆ Iron	254.75	v.s.	n.a.

5

Thermodynamics of Redox Rxns

◆ Thermodynamically favorable

◆ At pH = 0:



◆ At pH = 14:



◆ Highly energetic at extreme pH's

◆ Powerful oxidant at extreme pH's

6

Kinetics of Redox Rxns

- ◆ Kinetically Unfavorable
- ◆ Rule of Thumb: Rate of Oxidation Increases as the Oxidation Number of the Halogen Decreases
- ◆ $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- \ll \text{ClO}^- \sim \text{Cl}_2$
- ◆ $\text{BrO}_4^- < \text{BrO}_3^- \ll \text{BrO}^- \ll \text{Br}_2$
- ◆ $\text{IO}_4^- < \text{IO}_3^- < \text{I}_2$
- ◆ $\text{ClO}_4^- < \text{BrO}_4^- < \text{IO}_4^-$
- ◆ Rate Limiting Step : Cl - O bond scissoring
- ◆ Kinetically Stable, Thermodynamically Favorable

7

Production of Perchlorate

- ◆ Industrially: electrolysis of aqueous sodium chlorate to form sodium perchlorate
- ◆ All other perchlorate salts and perchloric acid are made from NaClO_4^- .
- ◆ NH_4ClO_4 is produced by an exchange process:
 - ◆ $\text{NaClO}_4^- (\text{aq}) + \text{NH}_4\text{Cl} (\text{aq}) \rightarrow \text{NaCl} (\text{aq}) + \text{NH}_4\text{ClO}_4 (\text{s})$
- ◆ At 200°C, NH_4ClO_4 bursts into flame
 - ◆ $2 \text{NH}_4\text{ClO}_4 (\text{s}) \rightarrow \text{N}_2 (\text{g}) + \text{Cl}_2 (\text{g}) + 2 \text{O}_2 (\text{g}) + 4 \text{H}_2\text{O} (\text{g})$

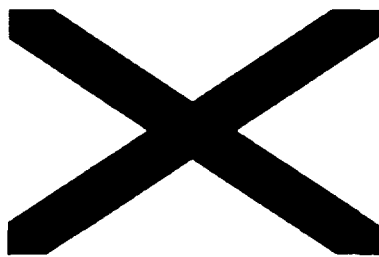
8

Analytical Techniques for Perchlorate Analysis

- ◆ **(In Aqueous Solution)**
- ◆ Liquid-Liquid Extraction
 - ◆ Nitron, Methylene Blue, Brilliant Green, Others
- ◆ Gravimetric Analysis
- ◆ Flame Atomic Absorption Spectrometry
- ◆ UV-Spectrometry
- ◆ Ion Pair High Performance Liquid Chromatography
- ◆ Ion Chromatography

9

Ion Chromatography



10

Perchlorate - Ion Chromatography Methods

- ◆ Pre-Jan 1997- Aerojet Method
 - ◆ MDL = 100 ppb
 - ◆ AS-9 column, NaOH in MeOH/H₂O, sulfuric acid
 - ◆ 35 μ L injection volume
- ◆ April 1997 to January 1998 AS-5 Method
 - ◆ California Department of Health Services
 - ◆ Modified Dionex method
 - ◆ Large injection loop volume (740 μ L)
 - ◆ p-cyanophenol, 120 mM NaOH
 - ◆ AMMS suppression, 35 mM sulfuric acid regenerant
 - ◆ Conductivity detector
 - ◆ MDL = 0.7 μ g/L
 - ◆ MRL = 4 ppb

11

Perchlorate- IC Methods (Cont'd)

- ◆ April 1998 - Dionex AS-11
 - ◆ Published in AEL, April 1998
 - ◆ Separation on AS-11 anion exchange column
 - ◆ Large injection loop volume (1000 μ L)
 - ◆ 100 mM NaOH, without modifier
 - ◆ ASRS auto suppression in external water mode
 - ◆ Conductivity detector
 - ◆ MDL = 4 ppb
 - ◆ 2 mM p-cyanophenol, 120 mM NaOH
 - ◆ AMMS suppression, 35 mM sulfuric acid regenerant
 - ◆ Conductivity detector

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Intra-Laboratory Performance of AS-5 and AS-11

◆	AS-5 *	AS-11 **
◆ MDL***	1 ug/L	0.25 ug/L
◆ MRL	4 ug/L	1 ug/L
Linear Range	2 - 100 ug/L	2 - 100 ug/L
◆ Spike Recovery	87-98 %	98-99 %
◆ Dup. Analysis	+/- 10%	+/- 10%

- ◆ * Okamoto, H. *et. al.* California Department of Health Services, Standard Operation Procedures: Determination of Perchlorate by Ion Chromatography, 3 Jun 1997.
- ◆ ** Jackson, P. *et. al.* American Environmental Laboratory, April 1998.
- ◆ ***Code of Federal Regulations 40, Chapter 1, Pt. 136, Appendix B

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Effect of pH on IC Response and Stability of ClO_4^-

- ◆ Examine the Stability of ClO_4^- with respect to pH
- ◆ Examine the Effect of pH on
 - ◆ Detector Response
 - ◆ Perchlorate Retention Time

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Stability Study - pH *

- ◆ Parameters
 - ◆ Perchlorate Concentration: 50 and 100 ppb
 - ◆ pH Levels: pH 5 and pH 9
 - ◆ Storage Conditions: 4°C and Room Temp.
 - ◆ Weekly Concentration Determination
 - ◆ Four Week Duration
- ◆ Method - AS-11 Modified
 - ◆ DX - 500 with Conductivity Detector
 - ◆ 58 mM NaOH in Deionized Water
 - ◆ 1 mL Sample Loop Volume

◆ * Contributors: Dickson, S. and Chaudhuri, S., UDOH/DELS

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Stability Study - pH

◆					Standard	
◆ pH	ppb.	Temp.	Mean	Deviation	%CV	
◆ 9	100	cold	98.5	4.2	4%	
◆ 9	100	r.t.	99.7	2.9	3%	
◆ 5	100	cold	97.5	4.6	5%	
◆ 5	100	r.t.	98.7	2.6	3%	
◆ 9	50	cold	47.0	1.8	4%	
◆ 9	50	r.t.	48.8	2.5	5%	
◆ 5	50	cold.	48.7	2.1	4%	
◆ 5	50	r.t.	48.5	2.6	5%	

- ◆ Between pH 5 and 9, perchlorate is stable beyond 30 days

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Effects of pH on Response and Retention Time

- ◆ Parameters
 - ◆ 50 ppb Perchlorate Prepared in Reagent Water
 - ◆ pH Range: pH 3.8 to pH 9.9 at 1 pH Interval
 - ◆ pH Range was Limited by Instrumentation
 - ◆ Triplicate Analysis
- ◆ Method - Modified AS-11
 - ◆ DX-500 with Conductivity Detector
 - ◆ 58 mM NaOH in Deionized Water
 - ◆ 1 mL Injection Loop Volume

◆ * Contributors: Dickson, S. and Chaudhuri, S., UDOH/DELS

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Effect of pH on Perchlorate Retention Time

◆	Mean	Standard	
◆ pH	(min.)	Deviation	%CV
◆ 3.8	12.2	0.01	0.1%
◆ 4.7	12.2	0.01	0.1%
◆ 6.0	12.2	0.03	0.2%
◆ 7.0	12.3	0.01	0.0%
◆ 8.3	12.3	0.01	0.1%
◆ 8.9	12.3	0.01	0.0%
◆ 9.9	12.3	0.01	0.0%

- ◆ No Retention Time Shift with Respect to Changing pH

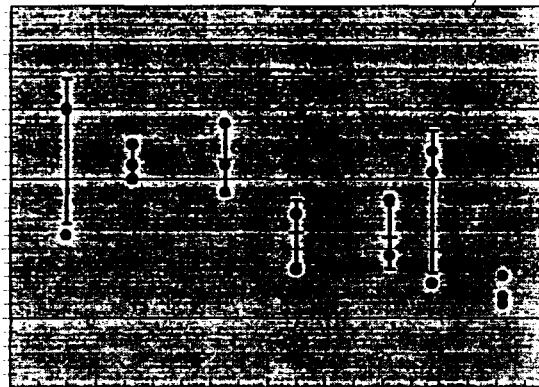
18

Effect of pH on Ion Chromatography Response

◆ pH	Mean	Std. Dev.	%CV
◆ 3.8	48.4	1.04	2.1
◆ 4.7	48.2	0.25	0.5
◆ 6.0	48.2	0.50	1.0
◆ 7.0	47.2	0.46	1.0
◆ 8.3	47.2	0.43	1.0
◆ 8.9	47.7	1.02	2.1
◆ 9.9	46.4	0.22	0.4

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Effect of pH on Ion Chromatography Response



Data
Mean

20

Effect of pH on Ion Chromatography Response

◆ Data Analysis - Linear Regression	
◆ Regression Statistics - Observations	21
◆ Multiple R	0.68850559
◆ R Square	0.47403995
◆ Adjusted R Square	0.44635784
◆ Standard Error	0.66160414
◆ ANOVA, N _o = No Correlation	
◆	
	<i>df</i> <i>SS</i> <i>MS</i> <i>F</i> <i>Sig. F</i>
◆ Regression	1 7.4957 7.4957 17.124 0.000559
◆ Residual	19 8.316681 0.43772
◆ Total	20 15.81238

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Effects of Methanol on IC Response and Retention Time

- ◆ Parameters
 - ◆ 50 ppb Perchlorate Prepared in Reagent Water
 - ◆ Methanol: 0 to 40%
 - ◆ Triplicate Analysis
- ◆ Method - Modified AS-11
 - ◆ DX-500 with Conductivity Detector
 - ◆ 58 mM NaOH in Deionized Water
 - ◆ 1 mL Injection Loop Volume

◆ * Contributors: Dickson, S. and Chaudhuri, S., UDOH/DELS

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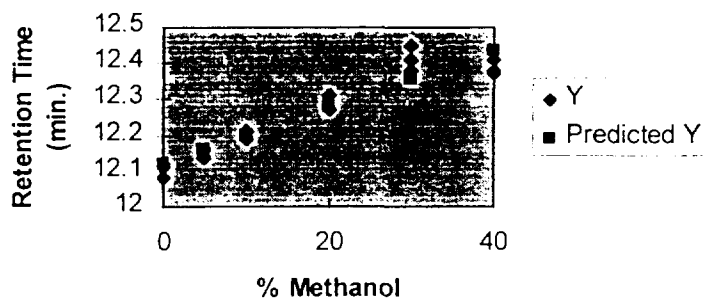
Effect of Methanol on Perchlorate Retention Time

◆ % Methanol	mean (min.)	std dev	%CV
◆ 0	12.10	0.021	0.2%
◆ 5	12.15	0.012	0.1%
◆ 10	12.20	0.012	0.1%
◆ 20	12.30	0.023	0.2%
◆ 30	12.41	0.035	0.3%
◆ 40	12.40	0.021	0.2%

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Effect of pH on Perchlorate Retention Time

Line Fit Plot - %Methanol vs RT



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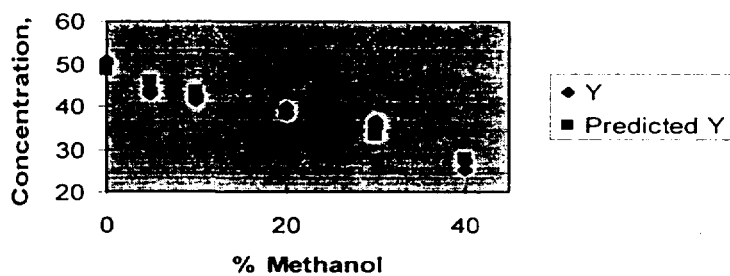
Effect of Methanol on Ion Chromatography Response

◆ % Methanol	mean (min.)	std dev.	%CV
◆ 0	50.50	0.346	0.7%
◆ 5	43.33	0.651	1.5%
◆ 10	41.93	0.702	1.7%
◆ 20	38.83	0.839	2.2%
◆ 30	35.77	0.862	2.4%
◆ 40	26.53	1.159	4.4%

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Effect of Methanol on Ion Chromatography Response

Line Fit Plot - % Methanol vs. IC
response



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Collaborative Study on Method Performance

- ◆ Parameters
 - ◆ [ClO₄⁻] Levels: 0, 5.8, 17.9, and 35.4 ppb
 - ◆ TDS Levels: 71, 142, and 284 ppm
 - ◆ Control: 50.8 ppb in Reagent Water
 - ◆ pH: 7.8 to 8.8
 - ◆ Container Types: Plastic and Glass
- ◆ Methods
 - ◆ AS-11 - 13 participants
 - ◆ AS- 5 - 4 participants
 - ◆ Two laboratories elected not to submit results

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Results on Method Performance Study (1 of 5)

◆ Sample	C1/T1	C1/T2	C1/T3
◆ [ClO ₄ ⁻], (ppb)	0.0	0.0	0.0
◆ TDS (ppm)	71	142	284
◆ pH	8.8	8.6	8.5
◆ Mean (ppb)	0.0	0.0	0.0
◆ Std. Dev.	NA	NA	NA
◆ Variance	NA	NA	NA
◆ %C.V.	NA	NA	NA

- ◆ All participants reported "non-detect."

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Results on Method Performance Study (2 of 5)

◆ Sample	S/T0 (Positive Control)
◆ [ClO ₄ -], (ppb)	50.8
◆ TDS (ppm)	0
◆ pH	7.7
◆ Mean (ppb)	51.79
◆ Standard Deviation	3.77
◆ Variance	14.19
◆ % Coefficient of Variation	7.3
◆ Prepared in reagent water	

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Results on Method Performance Study (3 of 5)

◆ Sample	C4/T1	C4/T2	C4/T3
◆ [ClO ₄ -], (ppb)	35.4	35.4	35.4
◆ TDS (ppm)	71	142	284
◆ pH	8.1	8.4	8.3
◆ Mean (ppb)	35.0	35.5	35.2
◆ Std. Dev.	2.36	2.88	2.80
◆ Variance	5.55	8.28	7.85
◆ % CV	7%	8%	8%

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Results on Method Performance Study (4 of 5)

◆ Sample	C3/T1	C3/T2	C3/T3
◆ [ClO ₄ -], (ppb)	17.9	17.9	17.9
◆ TDS (ppm)	71	142	284
◆ pH	8.4	8.5	8.5
◆ Mean (ppb)	18.0	17.8	17.9
◆ Std Dev.	1.43	1.54	1.59
◆ Variance	2.05	2.36	2.53
◆ % CV	8%	9%	9%

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Results on Method Performance Study (5 of 5)

◆ Sample	C2/T1	C2/T2	C2/T3
◆ [ClO ₄ -], (ppb)	5.8	5.8	5.8
◆ TDS (ppm)	71	142	284
◆ pH	8.0	8.0	8.0
◆ Mean (ppb)	5.7	5.7	6.0
◆ Std. Dev.	0.74	0.79	1.75
◆ Variance	0.55	0.62	3.05
◆ %CV	13%	14%	29%

- ◆ At low perchlorate concentrations, %CV increases with increasing amount of total dissolved solids

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Stability of Collaborative Study Samples

- ◆ Collaborative study samples in glass and plastic containers were stable up to eight weeks

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Anion Interference Study - AS-11

- ◆ 20 ppb ClO_4^- spiked with 100 ppb of each anion

- | | | |
|---------------|-------------|-------------|
| ◆ Arsenate | Arsenite | Bromate |
| ◆ Bromide | Carbonate | Chlorate |
| ◆ Chloride | Chromate | Cyanide |
| ◆ Humic Acid | Iodate | Iodide |
| ◆ Molybdate | Nitrate | Nitrite |
| ◆ o-Phosphate | o-Phthalate | Selenate |
| ◆ Sulfate | Sulfite | Thiocyanate |
| ◆ Thiosulfate | | |

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- ◆ Jackson, P., *et. al.* Perchlorate Interference Study on AS-11 column.

Anion Interference Studies - AS-11

◆ Method

- ◆ Dionex DX-500
- ◆ CD-20 Conductivity Detector
- ◆ GP-40 Gradient Pump
- ◆ AS40 Autosampler
- ◆ 1 mL Injection Loop Volume
- ◆ AS-11 (250 x 4.0), AG-11 (50 x 4.0 mm)
- ◆ Eluent: 100 mM NaOH
- ◆ Flow Rate: 1.0 mL/min

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Anion Interference Studies - AS-11

◆ Anion	Conc. ClO ₄ - (ppm)	Rec. (%)	◆ Anion	Conc. ClO ₄ - (ppm)	Rec. (%)
◆ Carbonate	50	96.6	◆ Sulfate	50	94.4
◆ Carbonate	200	98.8	◆ Sulfate	200	100
◆ Carbonate	600	92.1	◆ Sulfate	600	93.4
◆ Carbonate	1000	94.2	◆ Sulfate	1000	97.4
◆ Chloride	50	92.2			
◆ Chloride	200	99.2			
◆ Chloride	60	98.7			
◆ Chloride	1000	97.4			

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Anion Interference Studies - AS-11

- ◆ ClO_4^- retention time (9.0 min.) was unaffected by anions of interest
- ◆ ClO_4^- does not co-elute with anions of interest
- ◆ Only cyanide (4.38 min.), iodide (4.38 min.), and thiocyanate (6.27 min.) showed significant retention
- ◆ ppm levels of carbonate, chloride, and sulfate have no effect on perchlorate recovery

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Anion Interference Studies - AS-11

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Acknowledgement

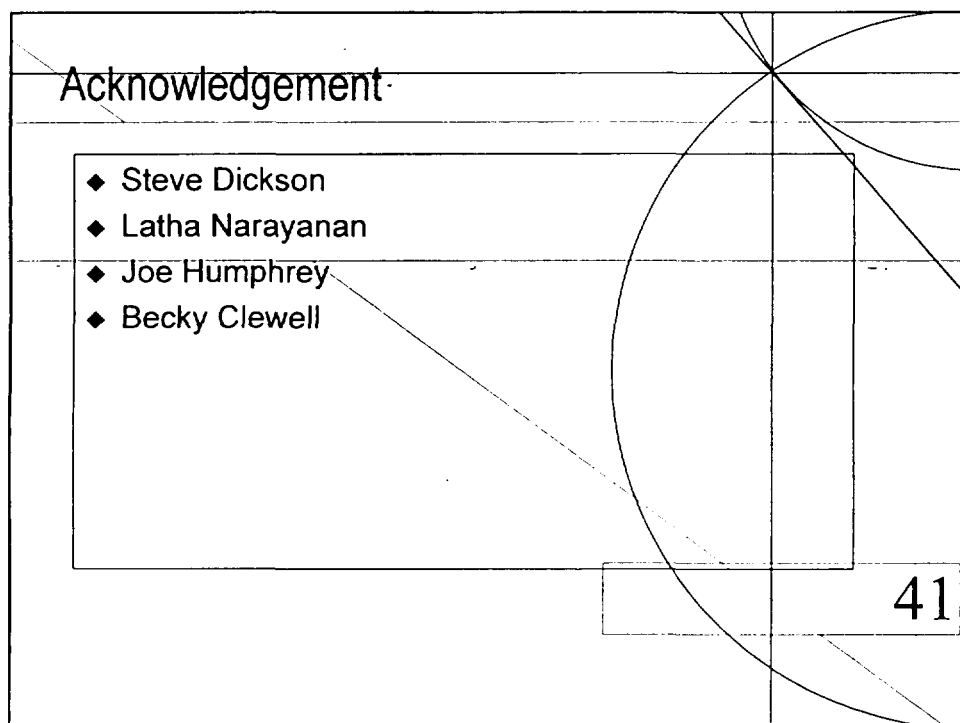
- ◆ Advanced Technology Laboratories
- ◆ AFRL/Operational Toxicology Branch
- ◆ American Pacific Corporation
- ◆ Applied Research Associates, Inc.
- ◆ Clayton Laboratory Services
- ◆ Dionex Applications Lab
- ◆ Metropolitan Water District of Southern California
- ◆ Montgomery Watson Laboratories
- ◆ Orange County Water District
- ◆ Science and Engineering

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Acknowledgement

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- ◆ Weck Laboratories
- ◆ Clinical Laboratory of San Bernardino San Bernardino, CA
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- ◆ State of California Department of Health Services
- ◆ Sanitation & Radiation Laboratories North Berkeley, CA

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Ecological Impact/Transport and Transformation of Perchlorate



Mr. Cornell Long, USAF

Dr. Ron Porter, USAF

Dr. Mark Sprenger, USEPA

Dr. Clarence Callahan, USEPA

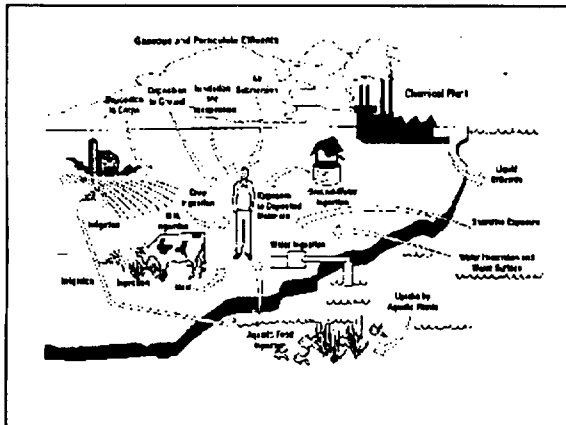


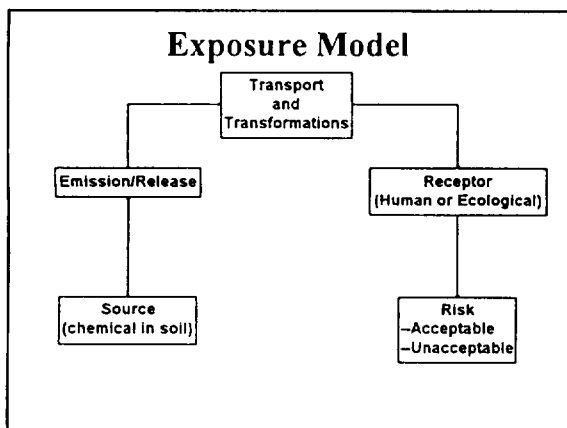
Introduction

- Background
- Fate and Transport of perchlorate
- Historical Studies
 - Potential ecological receptors
 - Observed Effects
- Proposed Activities and EPA Framework
- Discussion

Background

- Perchlorate salts have low volatility, but high solubility
- Solubility leads to high mobility in aqueous systems
 - Surface water
 - Groundwater
- Mobility and persistence may pose a threat to ecological receptors





Fate and Transport

(Transport and Transformation)

- What happens to perchlorate in the environment?
 - Physical characteristics
 - Attenuation processes
- What are the data gaps?



Physical Characteristics

- Vapor Pressure--no values found in literature
 - Volatilization not expected to be predominant pathway
- Density--1.95 g/mL
 - Will sink in water
 - Concentrated solutions also more dense than water

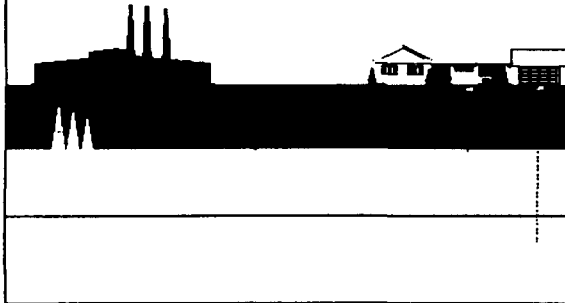
Physical Characteristics

- Solubility--20.2 g/100g solution
 - Dissolution expected and perchlorate ion will predominate in solution
 - Potential for potassium salt to precipitate--function of ion concentrations
- Standard potential--reduction for Cl from +7 oxidation state to -1
 - All values positive which indicates the reaction is thermodynamically favored

Physical Characteristics

- Standard potential
$$\text{ClO}_4^- + 4\text{H}_2 \longrightarrow 4\text{H}_2\text{O} + \text{Cl}^-$$
 - Little evidence that reaction occurs spontaneously
 - Reduction rate negligible at room temperature
 - Conclusion: Perchlorate is kinetically stable (most stable oxo-compound of chlorine)

Mobility of Perchlorate



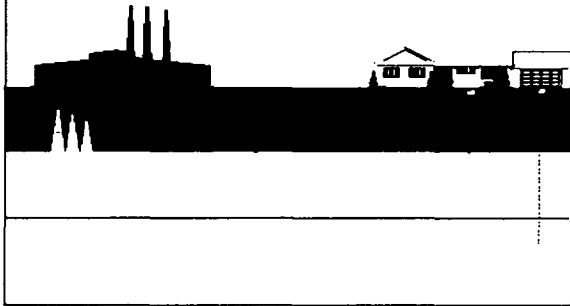
Attenuation Processes

- Dilution
- Precipitation
- Biological or chemical reduction
- Adsorption
- Ion-exchange

Attenuation Processes

- Dilution--concentrations expected to be significantly lower away from the source
 - However, function of the inert binder may influence source area concentrations
- Precipitation
 - Potassium less soluble, could lead to subsurface precipitation; long-term source area, near source area, and far source area re-dissolution

Mobility of Perchlorate



Attenuation Processes

- Biological or chemical reduction
 - Perchlorate reduction can occur at metal surfaces under acidic pH; however, inhibition by competing anions a problem
- Sorption
 - Perchlorate absorbs weakly to most soil minerals (NO_3^- and Cl^- more favorable)
 - Minimal impact inhibiting mobility

Summary

- Perchlorate is very soluble
- Very stable at low concentrations
- Very inert ion
- Some potential for precipitation in subsurface
- Reduction and sorption occurs to a lesser extent

Data Gaps General

- Binder Effects
 - Binder chemical degradation rates?
 - Leachability from binder?
 - Concentration of binder + other contaminants?
- Role of reduction and interaction of ClO_4 with subsurface soils

Data Gaps Site-Specific

- Soil properties
- Hydrology
- Infiltrating groundwater
- Characterization of leachates produced from source and near source soils

Contact

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Historical Studies of Perchlorate Effects

Dr. Ron Porter
Ecological Toxicologist
Human Systems Center
Brooks AFB, TX

The U.S. EPA Office of Emergency and Remedial Response (OERR), ie Superfund, has adopted a process for designing and conducting ecological risk assessments on chemical stressors at hazardous waste sites.

The heart of an ecological risk assessment is problem formulation. An effective problem formulation depends upon knowledge of contaminant fate and transport and either mechanism of toxicity and/or sensitive species

We know perchlorates:

- can affect mammalian and amphibian thyroid functioning
- can affect fish at high water concentrations
- can affect freshwater invertebrates at high water concentrations
- can affect plants

However, mechanism of toxicity is unknown

Outstanding issues for comprehensive problem formulation include:

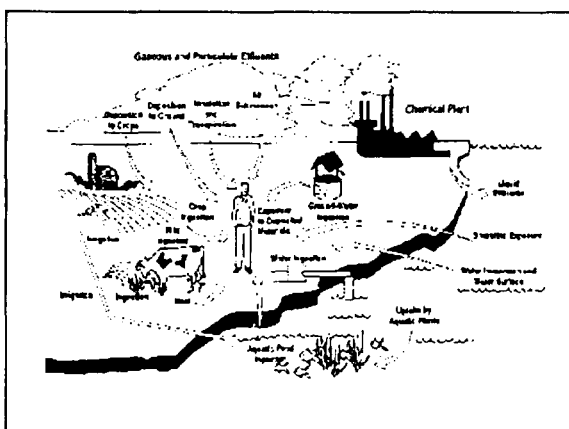
- further understanding of environmental fate and transport of perchlorate at low levels in environmental settings
- knowledge of perchlorate bioaccumulation potential and possible sequestering within organisms
- knowledge of possible toxicity mechanisms other than thyroid functioning
- evaluation of exposure mechanisms for ecological receptors

What are potential sources of additional information?

- Analytical techniques
 - limit the ability to evaluate bioaccumulation
 - limit the ability to evaluate sequestering in organisms
 - limit ability to evaluate exposure
- Use of high exposure toxicity tests

In Conclusion:

- The current approach to developing data on the ecological risks from perchlorate have conceptually followed Superfund's ecological risk assessment process.
- Because of the substantial knowledge and analytical limitations which currently exist, careful planning and a diligent problem formulation are critical to the successful evaluation of any potential ecological risk from perchlorate.



Ecological Receptors

- Aquatic biota
 - Sediment organisms
 - Aquatic plants
 - Aquatic vertebrates (fish)
 - Aquatic invertebrates (clams, crayfish, etc.)

Ecological Receptors (cont)

- Terrestrial biota
 - Soil organisms
 - Terrestrial plants
 - Terrestrial vertebrates (birds, mammals, etc.)
 - Terrestrial invertebrates (insects, spiders, etc.)

Ecological Receptors (cont)

- Agricultural products
 - Row crops
 - Livestock
 - Commercial fishing
- Food chain concerns
 - Recreational fishing
 - Fruits and nuts
 - Home gardens

Results of Data Search AP Acute Effects-Aquatic

- Ammonium perchlorate
 - Bacteria 100-1870 ppm (effect)
 - Algae 100 ppm (no effect)
 - Hydra 350-600 ppm (effect)

Results of Data Search AP Acute Effects-Terrestrial

- Corn (growth) 1-1000 ppm (effect)
- Cotton (seeds) 55 g/sq.m. (effect)
- Ryegrass (seeds) 55 g/sq.m. (effect)
- Soybean (growth) 1-1000 ppm (effect)
- Wheat
 - seeds 0.1-1000 ppm (effect)
 - growth 10 ppm (effect)

Data on Other Perchlorates

- Potassium perchlorate
 - Algae 79-360 ppm (effect)
 - Protozoan 23-1117 ppm (effect)
 - Daphnia 82-670 ppm (effect)
- Sodium perchlorate
 - Fish 3000-7000 ppm (effect)
 - Soybean 2.5-30 ppm (effect)

Data on Other Perchlorates (cont)

- Nitronium perchlorate
 - Fish 100-200 ppm (no effect)
 - Squash, peanut, corn 1000 ppm (no effect)

Results of Data Search

Chronic Effects

- No data for effects of ammonium perchlorate on terrestrial or aquatic plants and animals were found in the literature.
- Limited data for effects of potassium perchlorate were found in the literature
 - Two studies on the thyroid of lampreys
 - One study on growth and productivity of soybeans

Problem

What appropriate species of animals and plants and what assays are appropriate to evaluate potential ecological effects from exposure to ammonium perchlorate?

Proposed Screening Level

Bioassays

- | | |
|---|--------------------------------|
| • <i>Daphnia magna</i> or <i>ceriodaphnia dubia</i> | ⇨ Sediment invertebrate |
| • <i>Chironomus tentans</i> | ⇨ Larval sediment invertebrate |
| • <i>Hyallela azteca</i> | ⇨ Sediment invertebrate |
| • <i>Lemna minor</i> (duckweed) | ⇨ Vascular plant (aquatic) |
| • Fathead minnow | ⇨ Aquatic invertebrate |
| • Earthworm | ⇨ Soil invertebrate |
| • Microtox | ⇨ Bacteria (marine) |

Bioassays In Progress

1. <i>Agave</i> (100%)	1. <i>Agave</i> (100%)
2. <i>Agave</i> (100%)	2. <i>Agave</i> (100%)
3. <i>Agave</i> (100%)	3. <i>Agave</i> (100%)
4. <i>Agave</i> (100%)	4. <i>Agave</i> (100%)
5. <i>Agave</i> (100%)	5. <i>Agave</i> (100%)

Contact

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 Brooks AFB, TX 78235-5114
 210-536-6127 Fax 1130
 ronald.porter@guardian.brooks.af.mil

Interagency Perchlorate Steering Committee



Edward T. Urbansky
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Water Supply and Water Resources Division
Cincinnati, Ohio 45268



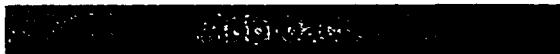
1

Treatment Technologies for Perchlorate Reduction



2

Treatment Technologies for Perchlorate Reduction



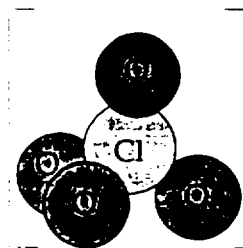
There is no one technique
that will work for every case.



There is no standard or benchmark
for evaluating performance.

3

Treatment Technologies for Perchlorate Reduction



1-

- An oxyanion of chlorine
- A strong oxidizing agent (thermodynamics)
- A very sluggish species (kinetics)

4

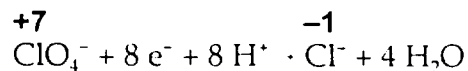
Treatment Technologies for Perchlorate Reduction

Name	Oxidation State	Formula
Perchlorate	+7	ClO_4^-
Chlorate	+5	ClO_3^-
Chlorite	+3	ClO_2^-
Hypochlorite	+1	ClO^-
Dichlorine	0	Cl_2
Chloride	-1	Cl^-

↑
Increasing
oxidizing strength

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Treatment Technologies for Perchlorate Reduction

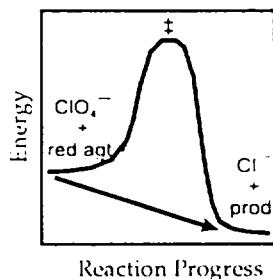


$$E^\circ = 1.287 \text{ volts}$$

A reducing agent transfers electrons to the chlorine atom in a perchlorate ion, converting it to chloride.

6

Treatment Technologies for Perchlorate Reduction



In general, perchlorate reduction is very slow even though perchlorate is a strong oxidizing agent.

Common reductants (e.g., thiosulfate, sulfite) show no measurable reaction.

7

Treatment Technologies for Perchlorate Reduction

A number of air-sensitive metal species can reduce perchlorate, but they cannot be used directly in water treatment because they are still too slow and their products would have to be removed.

Titanium(III)	Methylrhenium dioxide, CH_3ReO_2
Vanadium(II, III)	Dimolybdenum(III), Mo_2^{3+}
Chromium(II)	Molybdenum(III)
Ruthenium(II)	

8

Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction

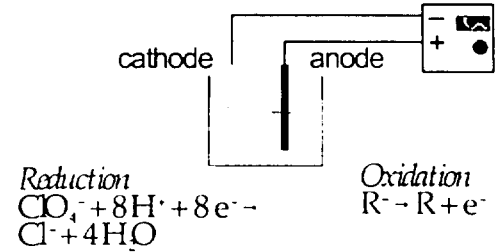
- Expense of materials
- Slowness of reaction
- Toxicity of by-products
- Removal of by-products



9

Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction

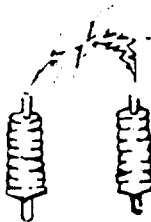


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Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction

- Tungsten carbide
- Ruthenium
- Platinum
- Aluminum
- Titanium
- Aluminum oxide
- Carbon (doped with Al_2O_3 or Cr_2O_3)



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Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction

- Advantages
 - Nontoxic by-products
 - Well-known technique
- Disadvantages
 - Construction/implementation expense
 - Operation expense (electricity)
 - Electrolysis of water
 - Slowness (reaction and diffusion)
 - Safety (high voltage)

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The use of biological organisms, especially bacteria, to chemically reduce perchlorate to other chemical species

Perchlorate-reducing bacteria

Ideonella dechloratans

Proteobacteria

Vibrio dechloraticans Cuzenove B-1168

Wolinella succinogenes HAP-1



USAF, Tyndall AFB, Florida

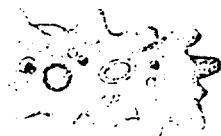
The bacterium *Wolinella succinogenes* is capable of using perchlorate as an oxidizing agent (electron acceptor) for metabolism.



The USAF and AF Research Labs have developed a bioreactor for this purpose.

- Advantages
 - Nontoxic by-products
 - Versatility
 - Speed

- Disadvantages
 - Acceptance
 - Regulatory barriers
 - Construction/implementation costs
 - Hardiness of bacteria



- Bacteria use a biological catalyst or enzyme, called a *reductase*, to reduce perchlorate.
- It may be possible to purify this enzyme and use it directly as a reactant for chemical reduction (addition or tethering).
- Perchlorate reductases evolved from nitrate reductases used by nitrogen-fixing bacteria (e.g., those in legumes).

■ Advantages

- No toxic perchlorate by-products
- Fast reaction time
- High effectiveness

■ Disadvantages

- High expense in producing enzyme
- High maintenance
- Difficult implementation
- Enzyme by-products unstudied

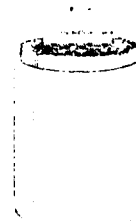


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■ Anion exchange

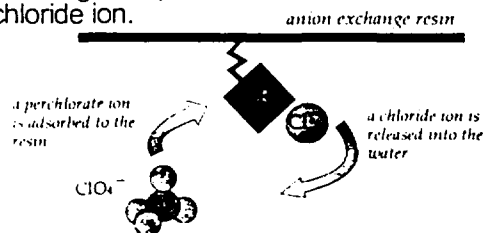
■ Membrane processes

- ▶ Nanofiltration
- ▶ Reverse osmosis
- ▶ Electrodialysis



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A positively charged resin is used to exchange the perchlorate ion for a harmless chloride ion.



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Oak Ridge National Laboratory
Oak Ridge, Tennessee



Selective pertechnetate (TcO_4^-)
removal to parts per trillion
($pg\ mL^{-1}$) levels

20

Anion exchange is used to remove nitrate from water.

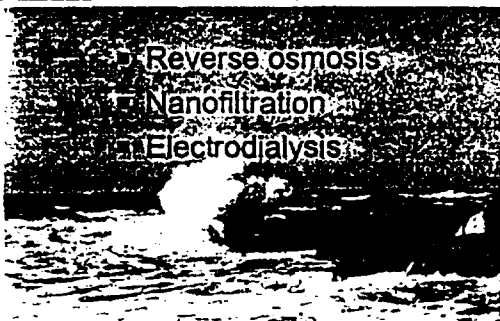


- Nitrate-selective resins already exist.
- Perchlorate and nitrate have similar physical properties (charge, size, aquation).
- Therefore, these resins are expected to be effective in removing perchlorate.
- However, permissible nitrate concentrations are much higher than the perchlorate action level.

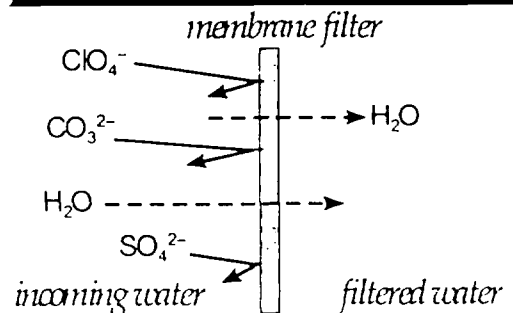
21

- Advantages
 - Reasonable operating costs
 - Well-developed technique
 - Easy implementation
 - Effectiveness
- Disadvantages
 - Waste disposal from regeneration
 - Moderate selectivity
 - Distribution system effects
 - Resin lifetime

22

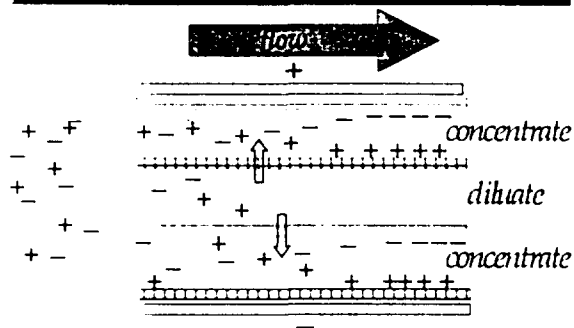


23



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Treatment Technologies for Perchlorate Reduction



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Treatment Technologies for Perchlorate Reduction

- Advantages
 - High effectiveness
 - Low operating cost
 - High throughput
 - Easy implementation



- Disadvantages
 - Low selectivity
 - Distribution system effects
 - Palatability
 - Waste effluent disposal

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Treatment Technologies for Perchlorate Reduction

- Reverse Osmosis and Nanofiltration
- Ozone/GAC (Chemical Reduction?)
- Biological Reduction
- Anion Exchange



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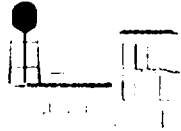
Treatment Technologies for Perchlorate Reduction

- Incomplete health effects studies
- Success at reaching trace concentrations
- Distribution system effects



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Treatment Technologies for Perchlorate Reduction



- Effects on other treatment processes
- Effects from other treatment processes
- Reliability

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Treatment Technologies for Perchlorate Reduction



- Palatability
- Time
- Expense



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Treatment Technologies for Perchlorate Reduction



The best solution for a specific situation is likely to be a combination of technologies.

- Anion exchange + bioremediation
- Nanofiltration + blending

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Treatment Technologies for Perchlorate Reduction

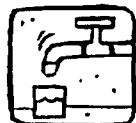
Small systems may benefit from a number of techniques that will not work in large systems.

- Reverse osmosis
- Anion exchange



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- Some techniques lend themselves to point-of-use devices.
- Both anion exchange and RO may be used at individual sites or for very small systems.
- No standards presently exist for purification systems; however, that could be rectified fairly quickly.



Congress has appropriated \$2 million to the East Valley Water District for studies on perchlorate.

The American Water Works Association Research Foundation has requested proposals.

EPA anticipates an initiative in fiscal year 2000.

- Perchlorate is unlike other contaminants already regulated.
- Effective management will require long and short term responses.
- The best solutions will only come about through continued cooperation among state, local, and federal agencies.



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James A. Hurley, Chemical Engineer

United States Air Force

Tyndall Air Force Base, Florida

Bachelor of Science degree in Chemical Engineering and Petroleum Refining from Colorado School of Mines, 1982.

Research chemical engineer, from 1982 to 1993, for the National Institute of Standards and Technology. Key programs include: investigation of high-pressure combustion characteristics of selected alloys of construction for the Space Shuttle Main Engine; development of novel reactor systems for chemical generation (excited-state oxygen, $O_2^1\Delta$) and for treatment of hazardous wastes (supercritical water oxidation, oxidation-reduction).

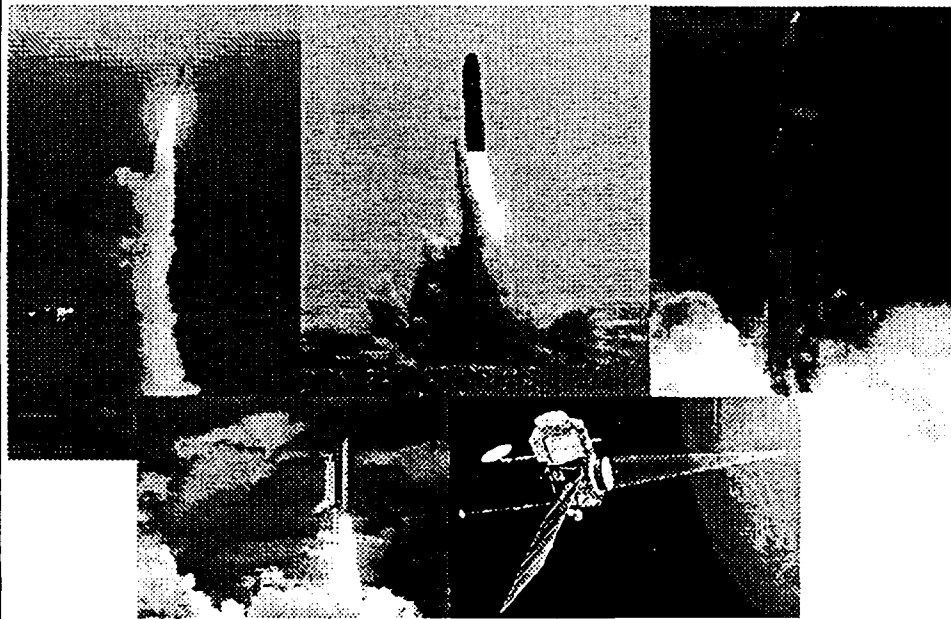
Technical Area Manager, from 1993 to present, developing chemical treatment technology for Air Force Research Laboratory, Materials and Manufacturing Directorate. Key programs include: Large Rocket Motor Demilitarization; Ammonium Perchlorate Treatment Technology, Air Force Industrial Waste Treatment, and Process Simulation and Chemical Systems Modeling.

Ammonium Perchlorate Treatment Technology Development

*James A. Hurley
AFRL/MLQE
Tyndall AFB, FL*



*Ammonium Perchlorate - A National Technical Asset
Integral to Strategic Defense Systems - ICBM, SLBM, NRO*





Peace Keeper 1st Stage (98,000 lb)

Requirement

➤ Increased Demand for Open-Burn/
Open-Detonation (OB/OD) Facilities
with Large-Rocket Motor Capacity.

- START II
- Nunn-Lugar
- Non-Proliferation Treaty
- Multi-National Force Reduction Treaty

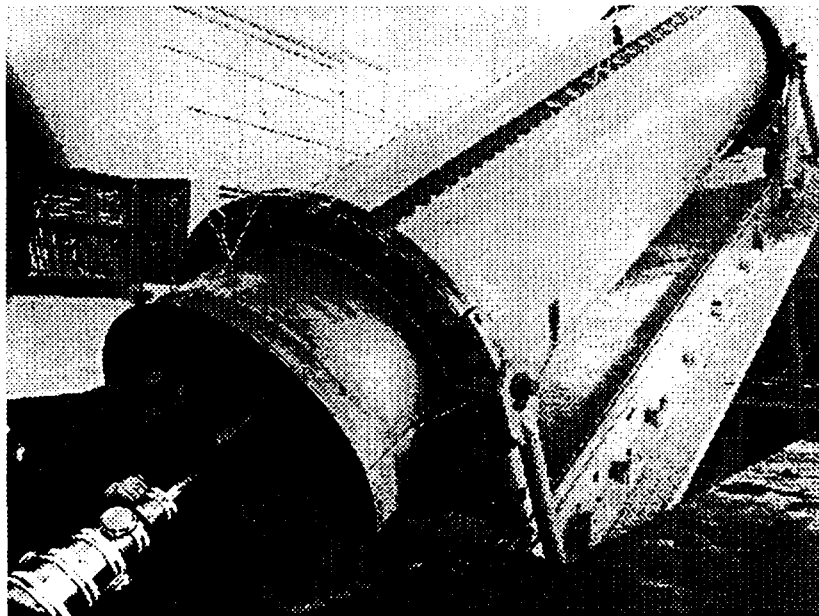
➤ Decreased Availability of OB/OD
Facilities.

- Clean Air Act Amendment - 1990 (CAAA)
- Base Realignment and Closure (BRAC)

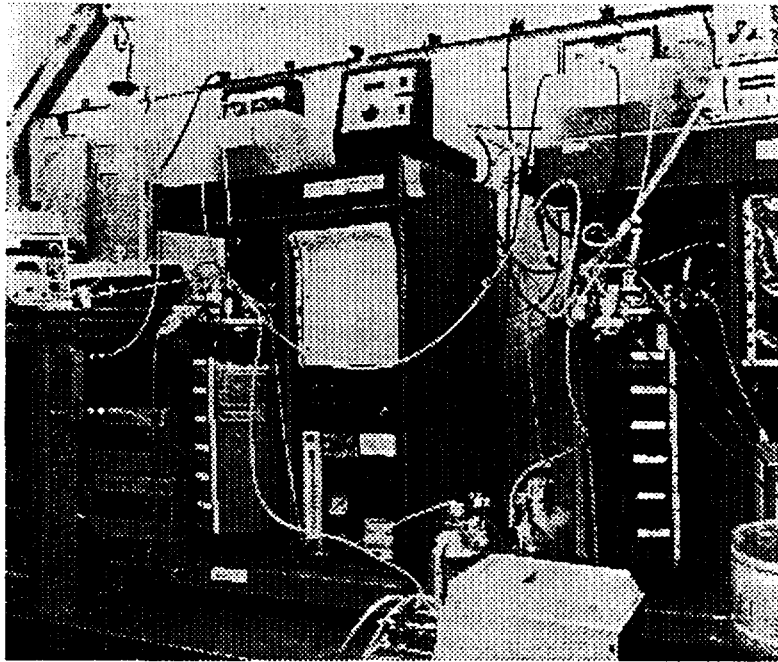
➤ Statement of Operational Need
(SON 003-90)

- Joint Logistics Commanders
- Gen McDonald- AFLC/CC

High-Pressure Water Washout of Solid Propellant



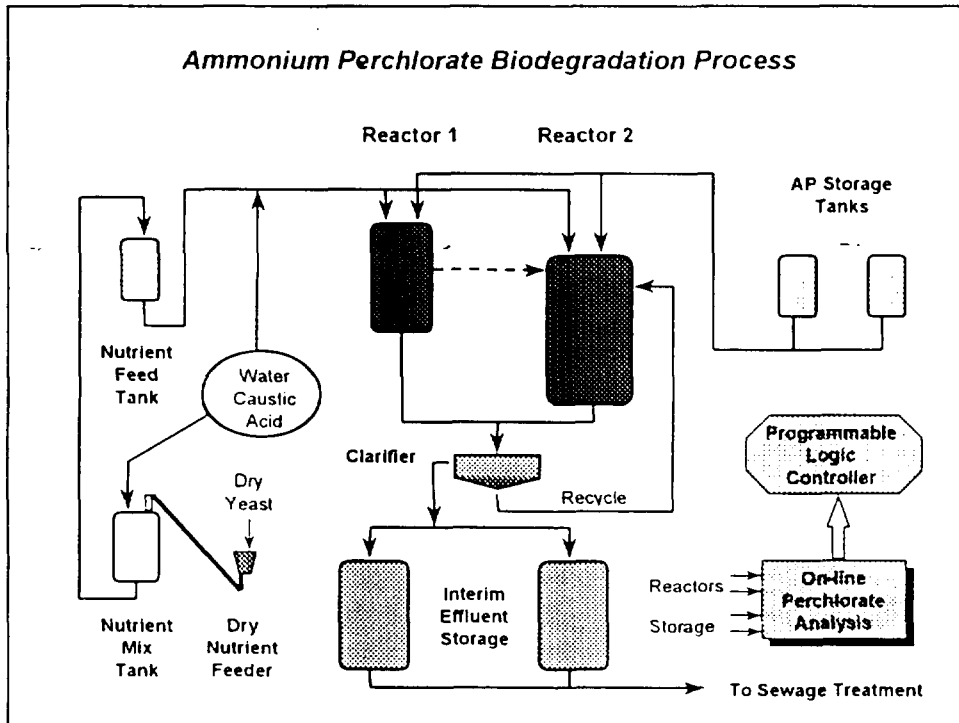
Bench-Scale Reactor System



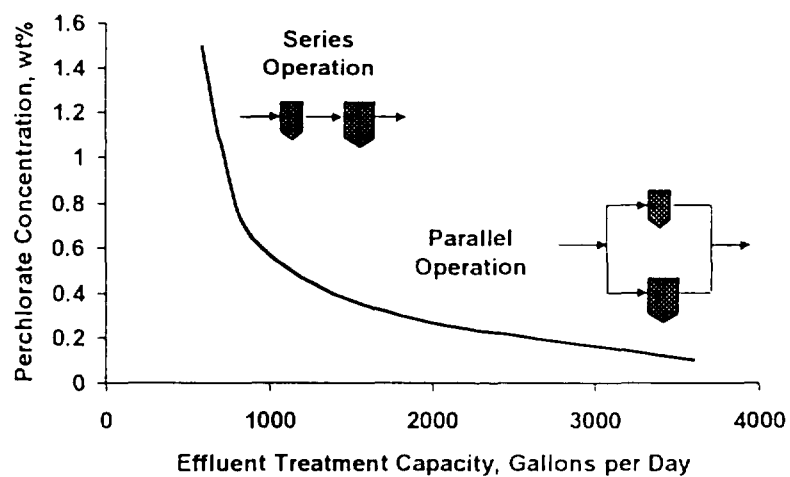
Production-Scale AP Reactor System

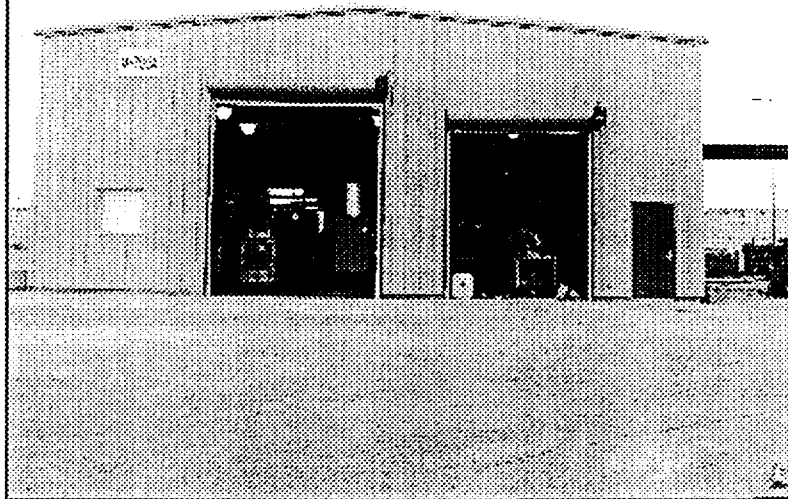


Ammonium Perchlorate Biodegradation Process

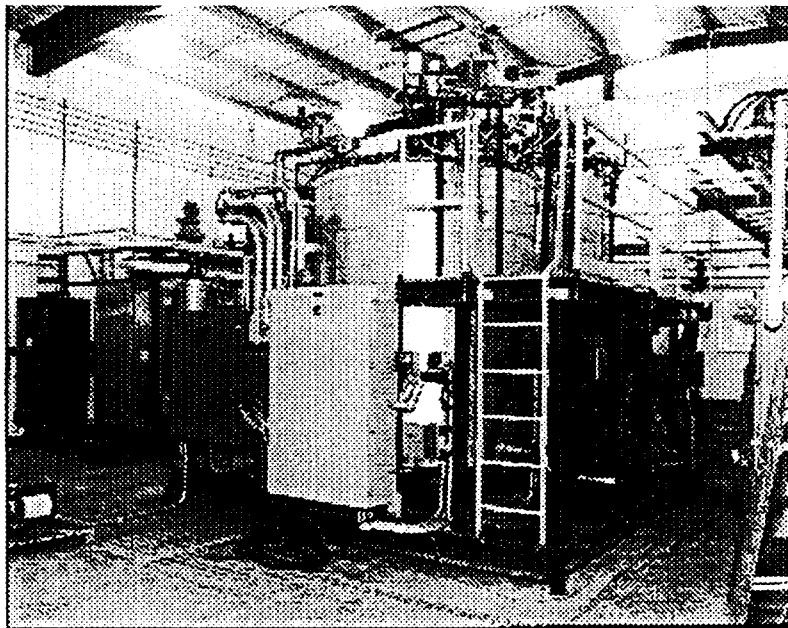


Effect of Perchlorate Concentration on Capacity



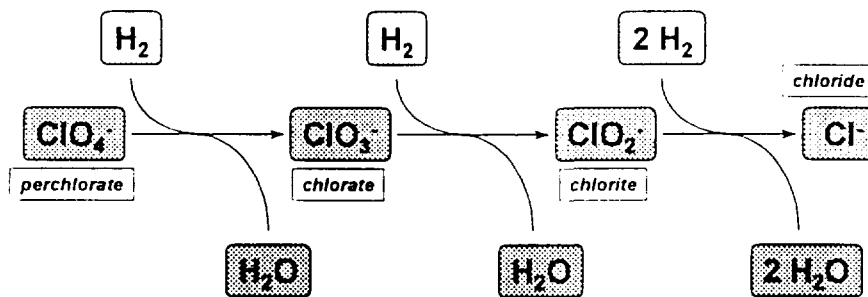


Building at Thiokol Housing the Ammonium Perchlorate Bioreactor System

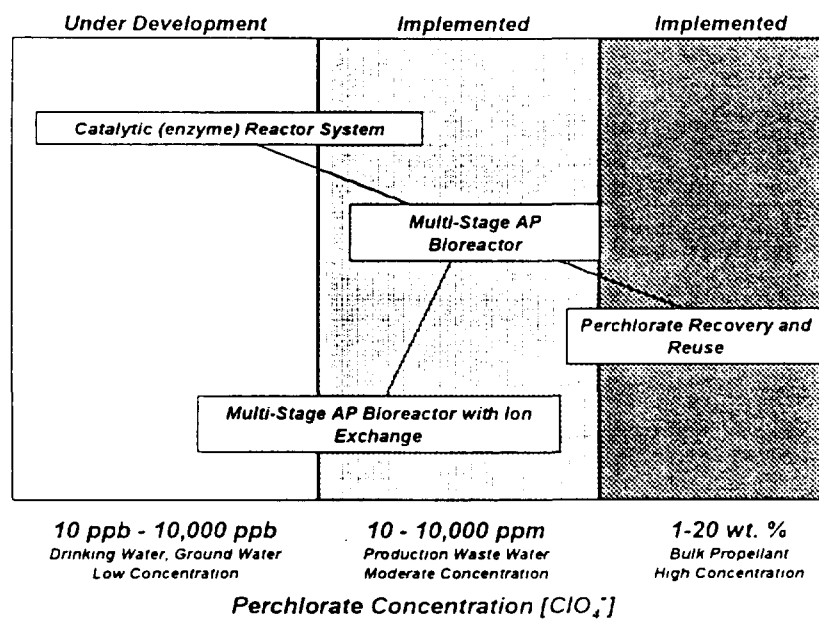


Primary and Secondary Ammonium Perchlorate Reactors

Metabolic Pathway for Energy Production in *Wolinella succinogenes* HAP1



AP Treatment Technology vs Process Requirement



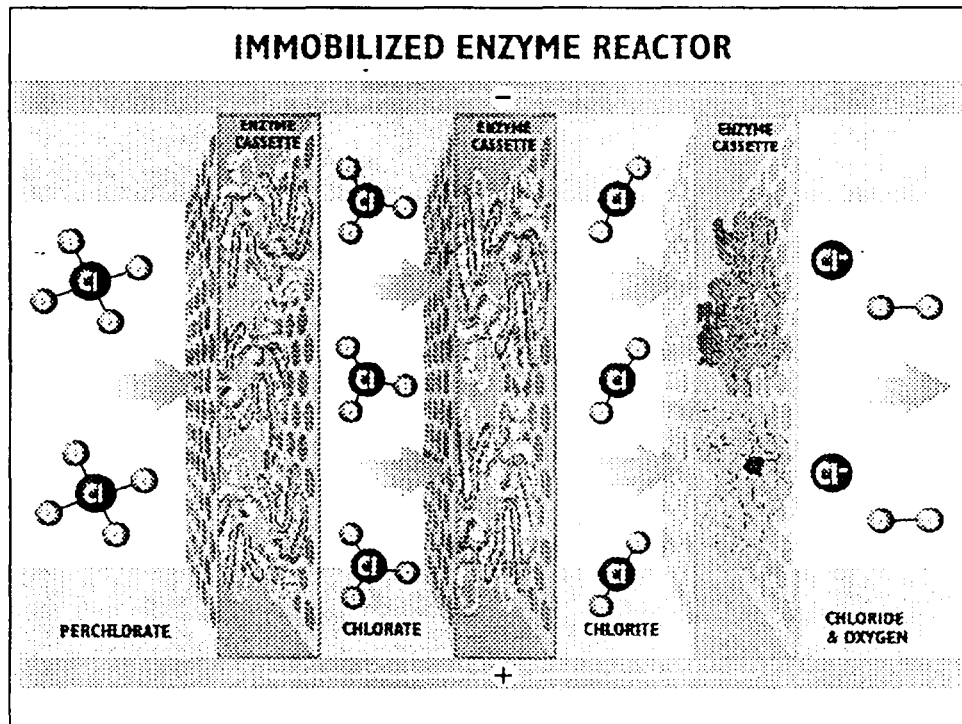
**Low-Concentration AP, High-Volume
Wastewater Treatment**

Two Approaches

- ❶ ***New (or Improved) Unit Operations Enabling Utilization of Demonstrated Moderate-Concentration AP Water Treatment***
 - ***Reverse Osmosis***
 - *Limited Capacity*
 - *Requires Effluent Reconditioning*
 - ***Capacitive Deionization***
 - *Small Electrochemical Driving Force Limits Capacity*
 - *Requires Effluent Reconditioning*
 - ***Ion Exchange***
 - *Resin Regeneration Very Difficult*
 - *Efficacy Uncertain at ppb Concentration Level*
 - *Selectivity Difficult*
 - *May Require Effluent Reconditioning*

**Low-Concentration AP, High-Volume
Wastewater Treatment (cont.)**

- ❷ ***New Process for Treating Low-Concentration AP Water Directly***
 - ***Conventional Catalytic Reactor System***
 - *Non-Selective*
 - *Mass-Transfer Limited*
 - *Unknown Kinetics, Unknown Efficacy*
 - ***Enzyme Catalytic Reactor System***
 - *Anion Specific Selectivity*
 - *High Capacity*
 - *Wide Application Range*
 - *Affect of Other Contaminants Unknown*
 - *Requires Multi-Disciplinary Effort*
 - *System Sustainability Uncertain*



Air Force Benefit

- *The payoff to the Air Force from this continued effort is reduction of weapon system operational cost as well as ensured continued sustainability.*
- *Manufacturing and maintenance facilities are under ever increasing constraints regarding the life-cycle management of materials used in weapon systems and their manufacture.*
- *Technology insertion opportunities are made possible by the continued participation of MLQ in Air Force unique materials selection, development, and management through the weapon system life-cycle.*

Points-of-Contact

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